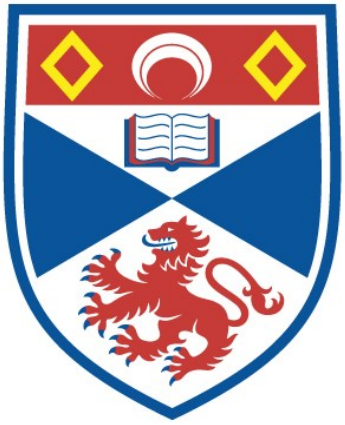
THE EFFECT OF VOLUME CHANGES ON THE ORDER-DISORDER TRANSITION IN SUBSTITUTIONAL ALLOYS

Archie Walter Ross

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE EFFECT OF VOLUME CHANGES ON THE ORDER-DISORDER TRANSITION IN SUBSTITUTIONAL ALLOYS.

being a thesis presented by

Archie Walter Ross, M.A.,

to the University of St. Andrews

in application for the degree of

Doctor of Philosophy.

1993

DECLARATION

I hereby declare that this thesis is based on the results of work carried out by me, that the thesis is my own composition and that it has not previously been presented for a higher degree.

February, 1957.

1925

CERTIFICATE

We hereby certify that Archie Walter Ross, M.A., has spent nine terms engaged in research work under our direction, that he has fulfilled the conditions of Ordinance No 16 (St. Andrews) and that he is qualified to submit this thesis in application for the degree of Doctor of Philosophy.

Research Supervisors.

February, 1957.

PERSONAL PREFACE

I matriculated in the University of St. Andrews in October, 1948 and graduated M.A. with Second Class Honours in Mathematics and Natural Philosophy in July, 1953. I am deeply indebted to the Department of Scientific and Industrial Research for the award of a Maintenance Grant which enabled me to commence research in the Department of Natural Philosophy in September, 1953, and to my supervisor, Dr. D. ter Haar, for his interest and encouragement throughout the period of my research, the result of which is described in this thesis.

I

INTRODUCTION

1 Among the many types of alloy there is one which is called a substitutional solid solution. An ideal substitutional solid solution of a metal A in a metal B is given when some of the lattice sites of the metal B are occupied by A atoms the lattice structure being unaltered. In the case where there are as many A atoms as B atoms in the alloy such an ideal solution would occur only if the A and B atoms were of equal size and if the pure A and B metals had the same type of lattice structure. In fact systematic investigation of metal alloys by many workers [1]) has shown that atoms whose atomic radii differ by more than about 15 per cent do not form extensive solid solutions. If the difference is less than this they form solutions over a wide range of composition. This rule is restricted by the condition that the atomic radii must be derived from monatomic phases with similar structures, and it should not be applied to alloys in which one of the constituents exhibits valence characteristics, e.g. bismuth, arsenic. In this work therefore we shall assume that, if an A-B alloy has a given type of lattice structure at the absolute zero, then, although thermal agitation may change the distribution of A and B atoms in the lattice, the lattice structure will not change with temperature irrespective of

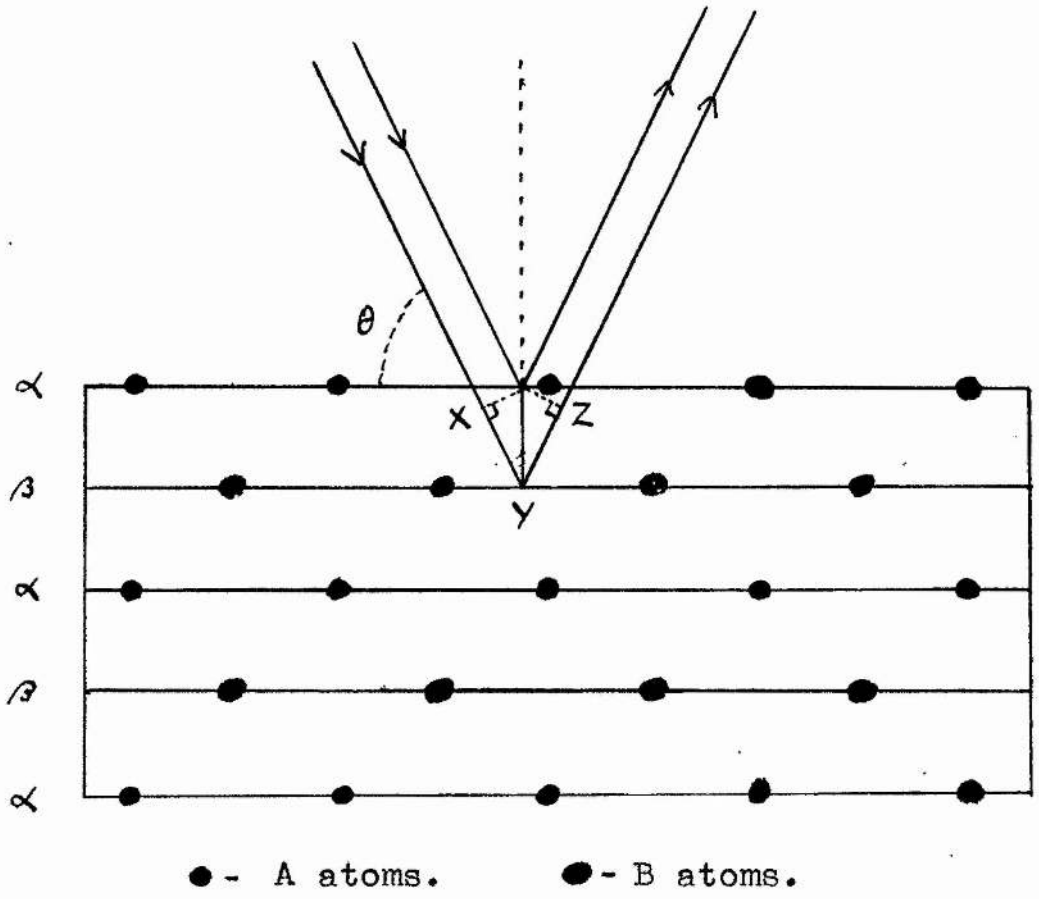
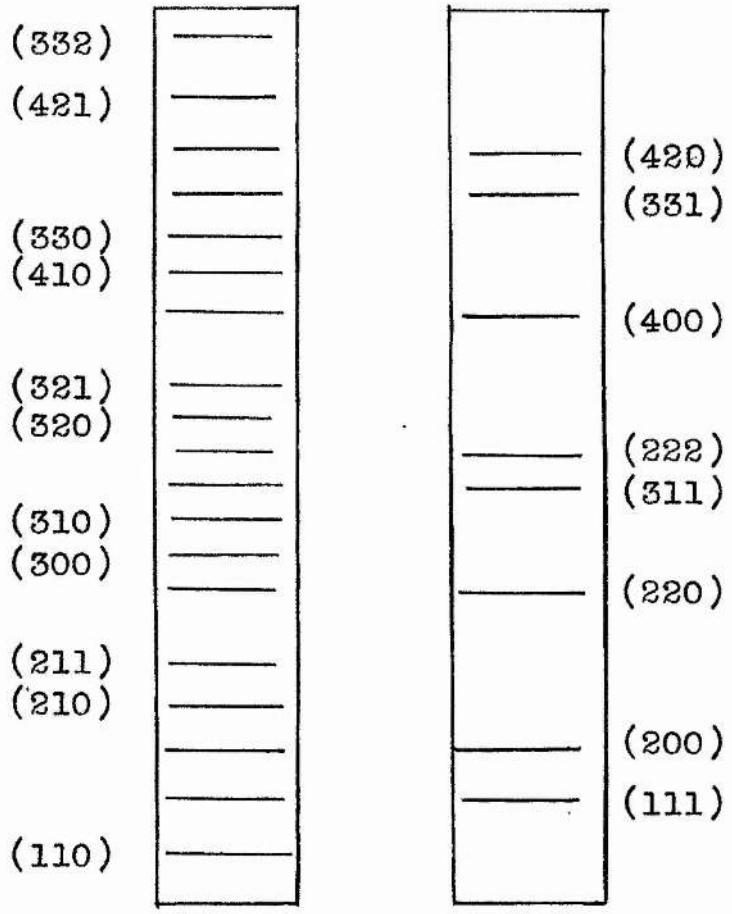


Figure 1.

the lattice types of the pure metals A and B. We shall return to this point in the next section.

Originally it was thought that the distribution of the atoms in a substitutional solid solution was of a purely random nature. Now, however, it is known that in a large number of cases the distribution is of a very definite nature, being similar below certain temperatures to the arrangement of the two elements of an ionic salt (e.g. rock-salt) in the crystalline form, and having a unique temperature dependence. The first indication that there exist ordered structures was given indirectly by chemical experiments carried out by Tammann [2]) in 1919. Investigation of copper-gold alloys showed that alloys containing more than fifty atomic per cent of copper were attacked by nitric acid which dissolved some of the copper but none of the gold, whereas those containing fifty atomic per cent or less copper were not affected. Tammann concluded from these results that the alloy CuAu had its atoms distributed over the lattice in an ordered manner; any extra copper atoms did not fit into the scheme and were easily removed. This evidence can hardly be considered conclusive however, as the alloy Cu_3Au, which has been investigated by Sykes and Jones [3]), possesses an ordered structure up to 664°A.

The most direct and conclusive evidence is provided by the analysis of X-ray diffraction patterns. Figure 1 rep-


(332)
(421)
(330)
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(222)
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(200)
(111)

Figure 2.

resents an X-ray beam impinging on a crystal lattice, the lattice sites being marked by circles. Let the angle θ be such that for rays impinging on the crystal planes denoted by α and β the path difference XYZ is equal to $n\lambda/2$ where n is an odd integer and λ is the wavelength of the X-rays. For a pure metal the reflecting powers of the two planes will be equal and as the reflected rays have opposite phase there will be no line on the X-ray spectrum in the direction θ. If the α-sites are occupied by A atoms and the β-sites by B atoms, and if the A and B atoms have quite different scattering factors, a line will appear on the spectrum. If there is a random distribution of equal numbers of A and B atoms over the lattice the reflecting powers of the α- and β-planes will again be equal (on average) and no line will appear. For intermediate degrees of order where the α-sites are predominantly occupied by A atoms and the β-sites by B atoms the different reflecting powers of the α- and β-planes will again give rise to a line with an intensity depending on the degree of order. Such a line is called a superstructure (or superlattice) line and its presence in a diffraction pattern shows the existence of a superstructure (or superlattice) in the crystal. Figure 2 is a drawing of X-ray diffraction patterns from Cu_3Au in a disordered state (right), and a well ordered state (left). The lines which appear on the left

and not on the right are the superstructure lines. The first observation of superstructure lines was by Bain [4] in 1923 working with the alloy Cu_3Au, this being a particularly favourable case because of the large difference in the scattering factors of the two elements. Improved techniques have enabled superstructure lines to be observed even in cases where the two elements are adjacent in the periodic table (e.g. β-brass: Cu-Zn)[5] and the more recent methods of neutron diffraction provide an even more sensitive means of detection.

All the superstructures which have been observed so far have an outstanding characteristic feature: in an A-B alloy A atoms tend to surround themselves by B atoms and vice versa. (We implicitly assumed this fact in discussing Figure 1 and it is a basic assumption in this work that the equilibrium state at the absolute zero is that which has the A atoms surrounded as completely as possible by B atoms and the B atoms surrounded as completely as possible by A atoms.) This fact must be taken into account by any theory of superstructures and this is usually done by describing the system in terms of a parameter, σ, called the short range order parameter, which is a measure of the degree to which each atom is surrounded by unlike neighbours. σ is usually defined in such a way that the best ordered arrangement is given by $\sigma=1$ and the worst by $\sigma=0$.

It is convenient to label the lattice sites as follows. Those lattice sites which at absolute zero are occupied by A atoms will be called α-sites and those occupied by B atoms will be called β-sites. We can now define a parameter, R, known as the long range order parameter, which describes the distribution of the A and B atoms over the α- and β-sites. (Many authors use S or s to denote the long range order but we wish to reserve the letter S to denote entropy.) R is defined in such a way that R=1 corresponds to the completely ordered distribution (all the A atoms on the α-sites) and R=0 to the distribution in which it is no longer possible to distinguish between the α- and β-sites. If there are equal numbers of A and B atoms, and hence of α- and β-sites, in the lattice, the value R=-1 also corresponds to a state of complete order since this value occurs when all the A atoms are on the β-sites and vice versa. This is a consequence of the similarity, in this particular case, between the α- and β-sites and it is quite sufficient to consider only positive values of R. We note that as R decreases σ must also decrease although not of course proportionally.

As the temperature is increased from the absolute zero thermal agitation will eventually cause atoms to change their positions in the lattice, that is will cause a reduction in the value of R. At the same time the tendency of

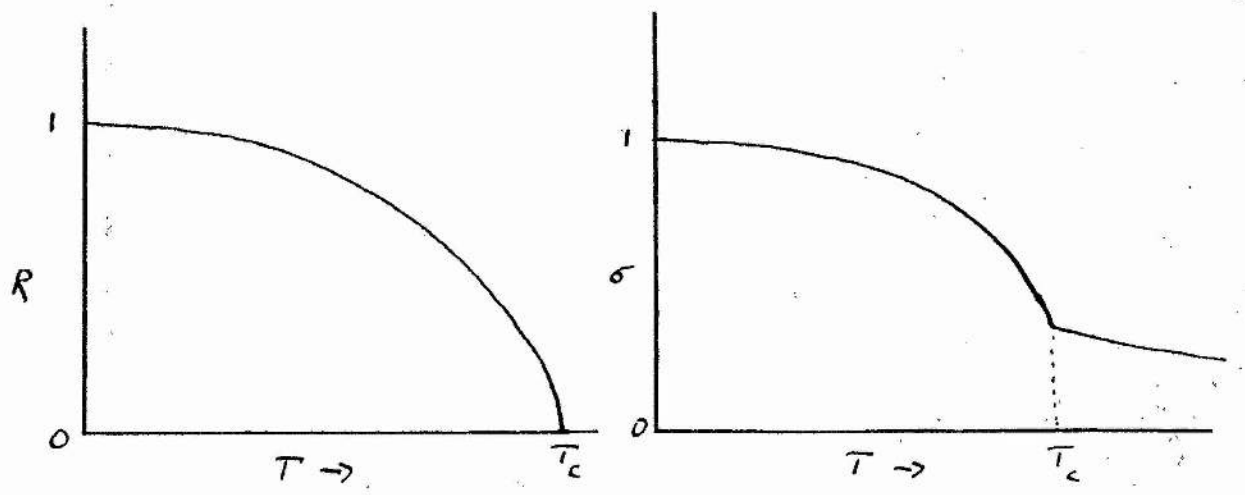


Figure 3a.

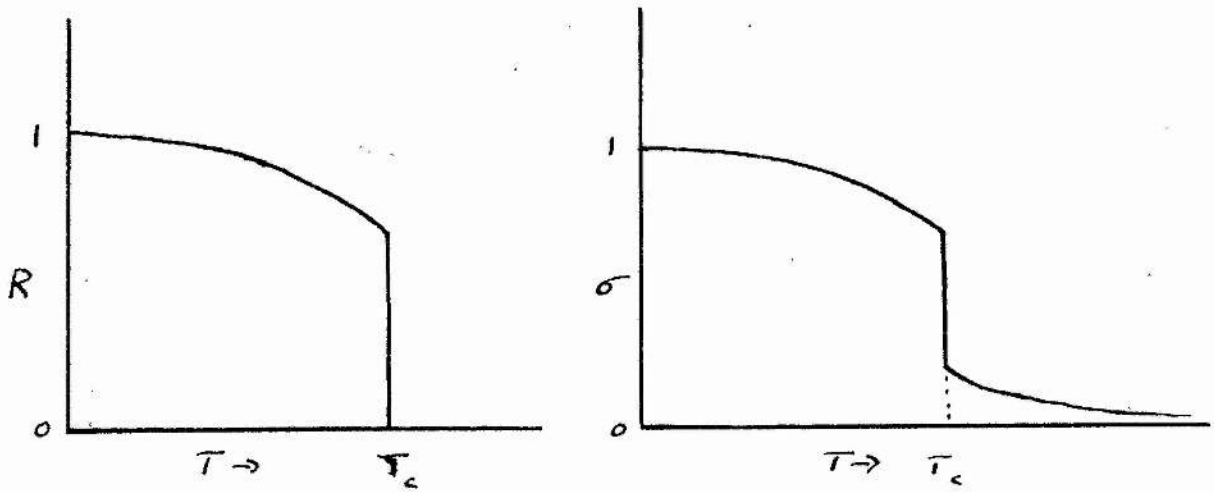


Figure 3b.

atoms to have unlike neighbours acts against this reduction (initially at anyrate). Thus at every temperature the system of atoms will be in a state of dynamic equilibrium maintained by the ordering tendency and the migration of atoms caused by thermal agitation, giving definite values to R and σ. As a reduction in σ implies a reduction in the ordering force we have here a situation where the disruptive influence increases as the temperature increases while the ordering force is reduced. Eventually a temperature is reached where the ordering force is no longer sufficient to counteract the effect of the migration of atoms due to thermal agitation and the distribution of the A and B atoms over the α- and β-sites becomes the random one, R=0. This temperature, in analogy with the theory of ferromagnetism, is called the Curie point of order or the transition temperature and will be denoted by T_c. Above this temperature the tendency of atoms to have unlike neighbours results in some small degree of local order which is gradually reduced as the temperature rises. Figure 3 shows two possible variations of the order parameters with temperature.

It is the tendency of atoms to have unlike neighbours which puts the phenomena of order in alloys into the general class of co-operative phenomena. Physical systems exhibiting such phenomena consist of sub-systems (in our

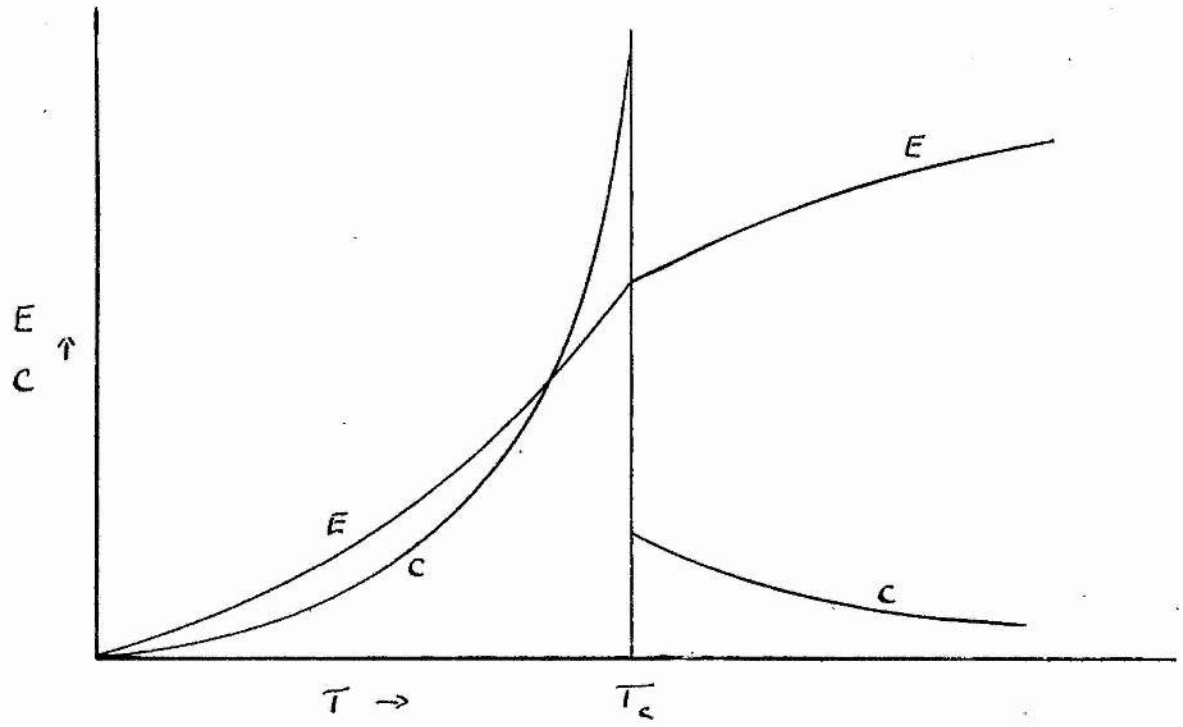


Figure 4a.

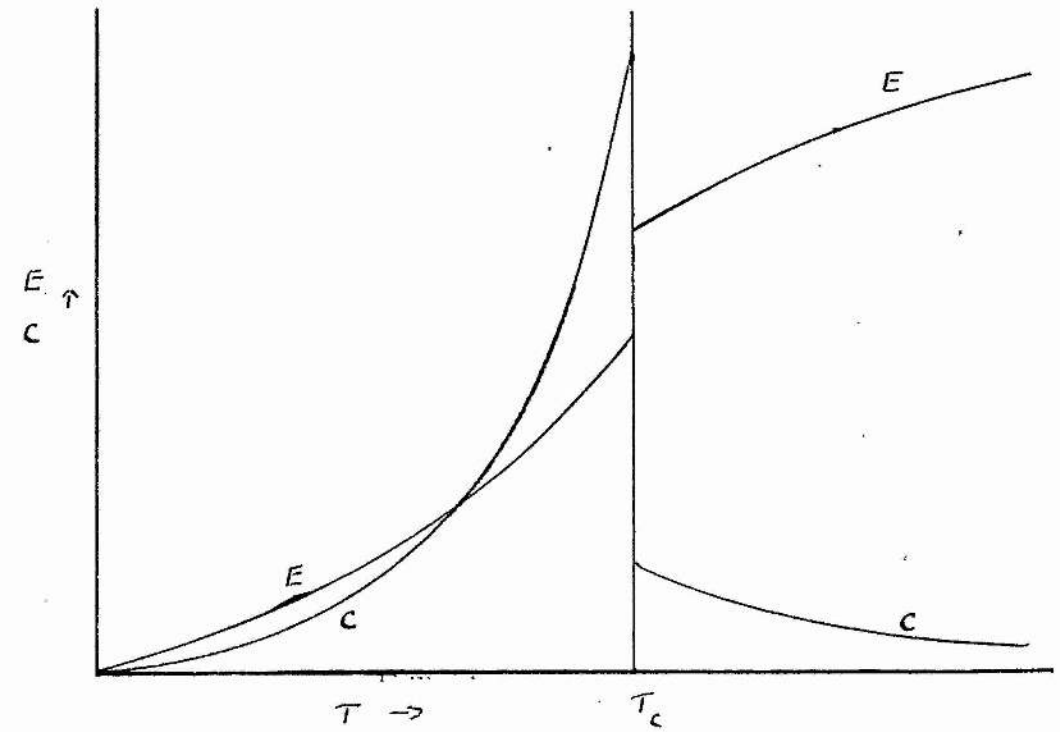


Figure 4b.

case atoms with a preference for unlike neighbours) which act on one another in such a way as to produce the co-operative effect (in our case a superstructure), the magnitude of the effect being a measure of the degree of co-operation between the sub-systems. We mention in passing that under certain conditions the discussion of substitutional alloys can apply equally well to the problem of ferromagnetism; the transition is made simply by altering the significance of the unit of energy [6,7].

2 Order in substitutional alloys gives rise to effects other than the production of superstructure lines in an X-ray diffraction pattern. In order to raise the temperature of the system we must supply energy to it. Part of this energy is required to produce disorder in opposition to the ordering force while the rest raises the temperature of the system in accordance with the appropriate normal specific heat law. Thus there is an excess energy in the system depending on the distribution of the A and B atoms over the lattice: this excess energy is usually called the configurational energy and it gives rise to an anomaly in the specific heat of the system. Figure 4 shows the temperature variation of the configurational energy and of the configurational specific heat for systems whose behaviour is represented by the curves of Figure 3. Figure 4b corresponds to Figure 3b and in this case there

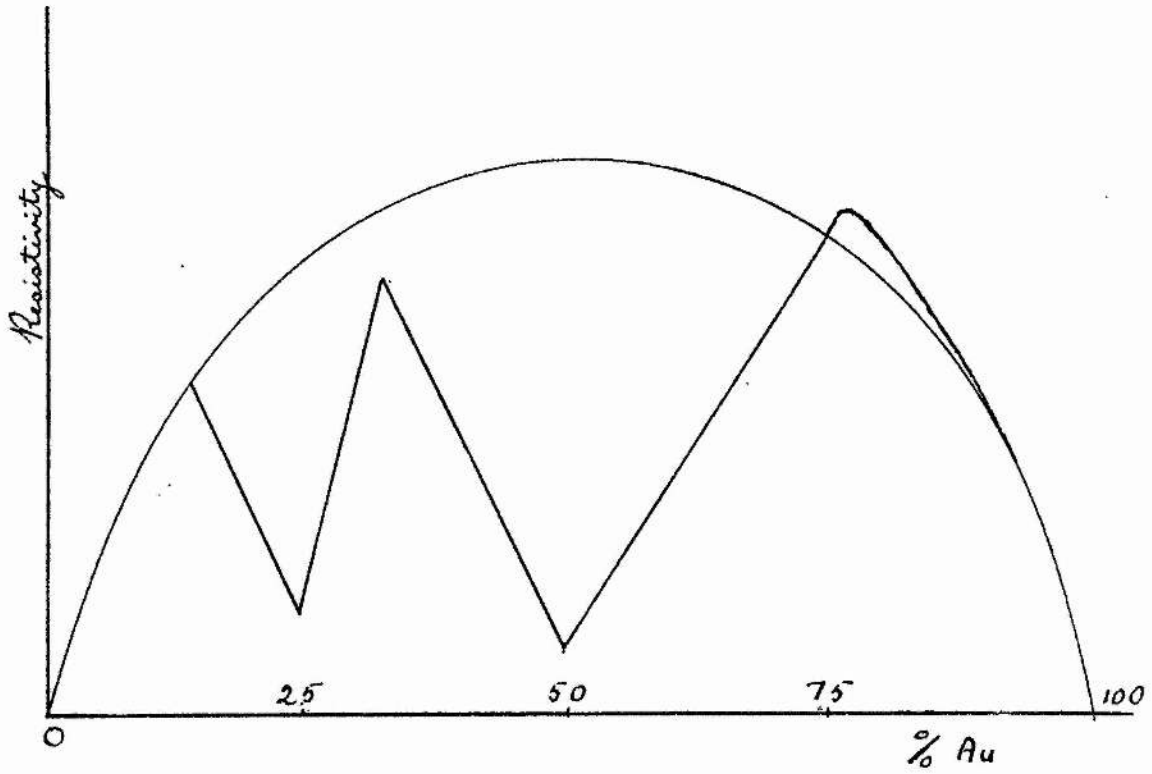


Figure 5.

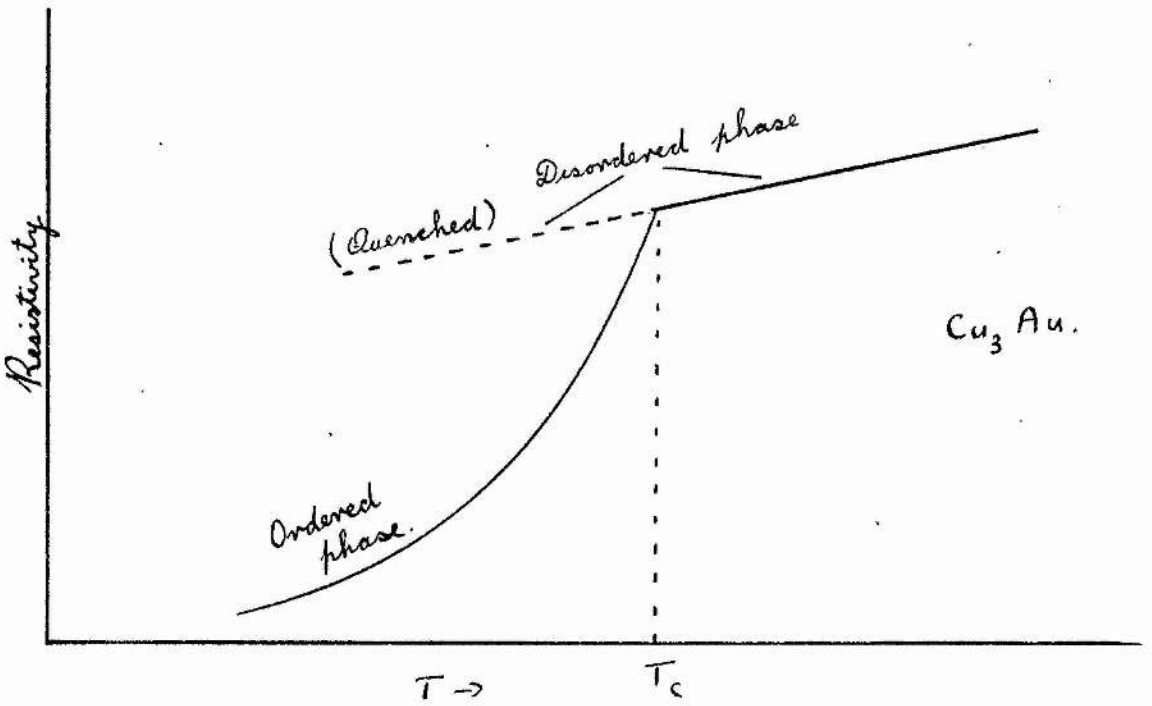


Figure 6.

is a latent heat as well as the lambda anomaly in the specific heat.

The electrical resistivity of an alloy is found to be dependent on its state of order. An alloy which has been rapidly quenched from a temperature above its transition temperature will have the state of order R = 0 frozen into it. There will certainly be no large volumes of the system characterised by high values of R. The electrical resistivity of an alloy in this state can be contrasted with the resistivity of the alloy after annealing at a temperature low enough to correspond to high degree of long range order but high enough to enable the atoms to arrange themselves accordingly. Figure 5 shows the variation of the electrical resistivity with composition of copper-gold alloys which have been subjected to these two treatments. The smooth curve is obtained for alloys quenched from 650°C and the other for alloys annealed at 200°C. The resistance minima of this second curve occur at the compositions CuAu and Cu_3Au, compositions for which superlattices are known to exist. Figure 6 shows the variation of the electrical resistivity of the alloy Cu_3Au with temperature.

A qualitative explanation of these effects can be given as follows. A perfectly periodic lattice offers zero resistance to the flow of electrons, electron scattering, and hence resistance, being produced by departures from

perfect periodicity. Such departures may be produced in several ways of which two are relevant to this discussion: 1) Thermal agitation will cause a displacement of the atoms from their mean positions giving rise to phonon scattering. The resistance due to this effect is denoted by ρ_1. 2) The presence of a foreign atom on one of the lattice sites will cause a departure from perfect periodicity at that point. This gives rise to impurity scattering, the resistance due to this effect being denoted by ρ_2. We assume that the resistance of the alloy is given by $\rho = \rho_1 + \rho_2$. This assumption will be valid to a first approximation (it is just Matthiessen's rule) although departures from this rule occur when higher approximations are taken into account [8]). In a completely disordered alloy ρ_2 is independent of temperature (there are exceptions to this rule, e.g. constantan, CuNi, but the variation with temperature is small) and can be considered as the resistance of the alloy at the absolute zero, that is, as the residual resistance. A theoretical treatment of the electrical resistivity of a disordered alloy was given by Nordheim [9]) in 1939. If the alloy consists of two metals A and B in the ratio x:(1-x) a straightforward calculation showed that the impurity scattering was proportional to x(1-x) and hence $\rho_2 \propto x(1-x)$. The smooth curve in figure 5 lies very close to this form.

In a completely ordered alloy, however, ρ_2 should theoretically vanish and in fact extrapolation to the absolute zero shows that the residual resistance of an ordered alloy is much smaller than that of the disordered alloy. This would account for the pronounced minima in Figure 5. We have still, however, to consider a possible dependence of ρ_1 on the state of order of the alloy. Detailed calculation shows that ρ_1 depends on the density of states and on the Debye characteristic temperature both of which may be expected to vary with the state of order of the alloy. In fact, for the Cu_3Au alloy, it has been found that T_D is greater in the ordered state than in the disordered state, leading to a reduction in ρ_1. That there is not a minimum of resistance in Figure 5 at the composition $CuAu_3$ (where the ordered state should give a reduced value of ρ_2) is presumably due to an increase of ρ_1 on ordering which is more than enough to counteract the decrease of ρ_2.

For a partially ordered alloy Muto [10]) in 1936-37 used the Bragg-Williams approximation (discussed in section 3) to obtain ρ_2 as a function of R, and found $\rho_2 = A+BR+CR^2$, A, B and C being temperature dependent. In several cases this relation is in reasonable agreement with experiment.

In 1929 Vogt and Seemann [11]) reported that the magnetic properties of Cu_3Au and CuAu were influenced by the degree of order in the alloys. Further work demonstrated that in

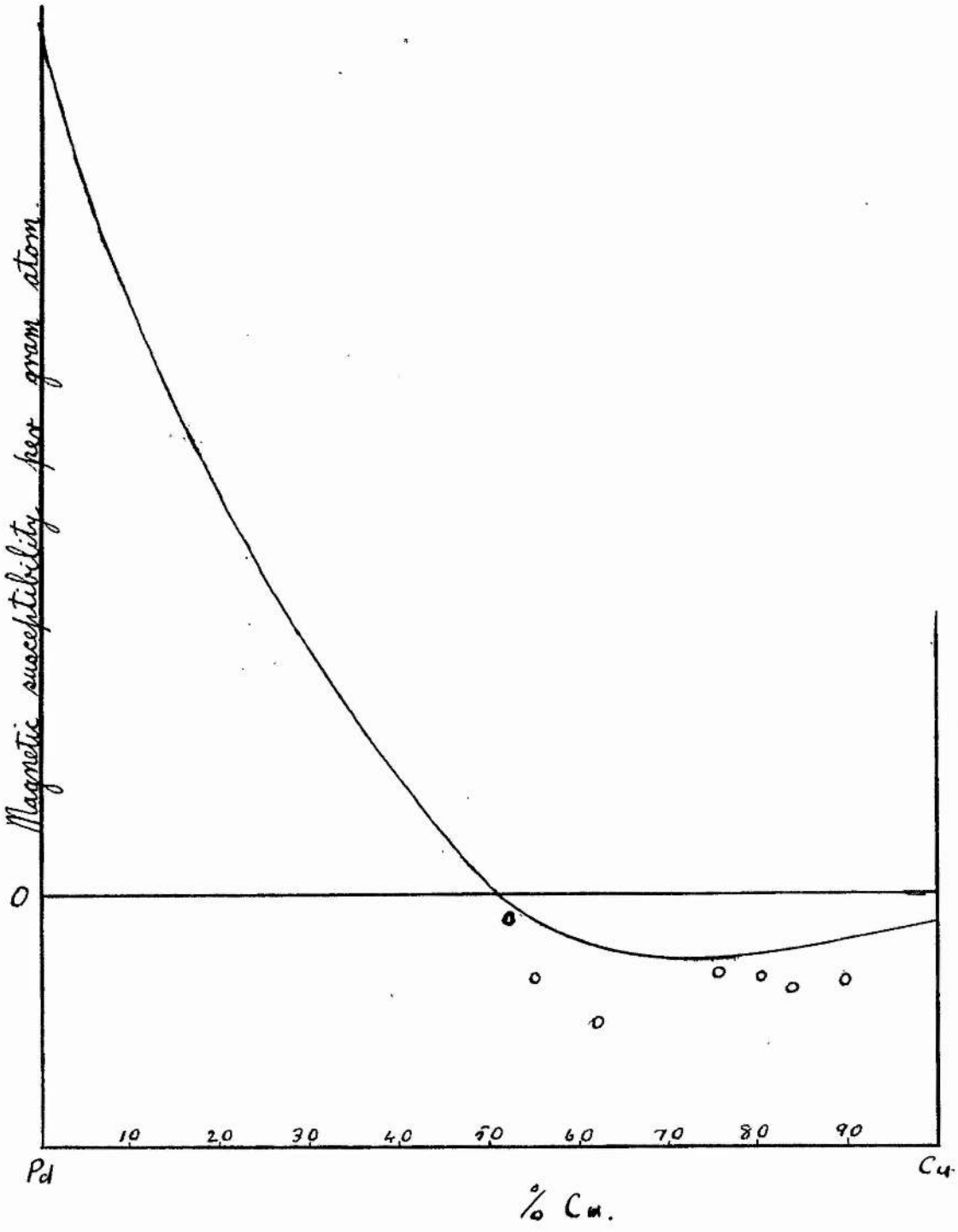

Magnetic susceptibility per gram atom
0
10
20
30
40
50
60
70
80
90
Pd
Cu
% Cu.

Figure 7.

some cases the diamagnetic susceptibility of a copper-gold alloy was increased on ordering and in other cases it was decreased. The measurements were carried out for only two states, one being assumed completely disordered and the other well ordered, and it is not known how the susceptibility behaves as a function of the order.

The behaviour of the magnetic susceptibility, χ, unlike that of the electrical resistivity, cannot be explained in general terms since it is strongly dependent on the types of atoms in the alloy and on the concentration. Figure 7 shows the dependence of χ on composition for the copper-palladium alloys. The smooth curve is for the quenched alloys and the circles represent values from the annealed specimens. It can be seen from this graph that for alloys in the region CuPd the change in χ on ordering is very small whereas the change in the resistivity is very marked in this region. This may be contrasted with the behaviour in the region about 17 atomic per cent palladium where the maximum degree of order, as shown by X-ray measurements, coincides with the maximum effects of ordering on both χ and ρ_2.

The smooth curve on Figure 7 can be understood as follows. Palladium metal is strongly paramagnetic and is known to have about ·55 holes per atom in the d shell. Copper has one more electron outside an inert gas shell than has

palladium (11 to 10) and as a first approximation we may consider the addition of copper to palladium as leaving the lattice unchanged and as increasing the number of electrons by one for every atom of copper added. The density of states in the d band of palladium metal is much greater than that in the s band and nearly all the extra electrons will go into the d band until it is filled up. Hence one would expect that when a copper-palladium alloy contains about 55 atomic per cent copper the magnetic susceptibility of the alloy should drop to zero. As can be seen from Figure 7 χ drops to zero when the amount of copper present is just over 50 atomic per cent. Alloys containing more than 55 atomic per cent copper would be expected to become more and more diamagnetic until the value appropriate to pure copper is reached. It is not obvious why there should be a minimum at a concentration of about 62 atomic per cent copper. To explain the further drop in χ ordering it is necessary to take fully into account the effect of concentration and order on the band structure and density of states and as far as we know this has not been done.

It was observed by Johansson and Linde [12]) that the lattice of the alloy CuAu changes from cubic above the transition temperature to tetragonal below. The axial ratio increases from 1·067 at T_c to 1·080 at temperatures

low enough for the alloy to be in a highly ordered state. Borelius [13]) assumed that it is the ordering which is responsible for this effect and used the axial ratio as a measure of the degree of order. It has been found, however, that both the cubic and tetragonal structures can exist together below the transition temperature, and as this type of behaviour is by no means the most common one we feel justified in treating only those cases covered by the assumption mentioned at the beginning of section 1.

One would not expect the equilibrium distance between two atoms to be independent of the choice of the atoms and thus it is reasonable that a lattice whose nearest neighbour pairs are entirely AB pairs should have a lattice parameter different from that of a lattice whose nearest neighbour pairs are equally likely to be AB or AA or BB pairs. From this it follows that the ordering process should be accompanied by a change in lattice parameter, that is by a change in volume, and this is indeed found to be the case. The ordering phenomenon in alloys is almost always accompanied by a diminution in volume. Since volume changes can be measured with a high degree of precision, accurate measurements could prove valuable as a measure of the degree of order. It is the purpose of this work to investigate the relationship between the lattice parameter and the degree of order on the basis of certain assumptions

about the inter-particle forces. In the discussion of the configurational energy on page 7 we tacitly assumed that the co-operative effect could be separated from the normal temperature effects and the first part of this work makes use of this assumption. In a later chapter we discuss the influence of lattice vibrations on the co-operative effect.

3 Before we proceed to describe and apply our model we shall give a brief resumé of the theoretical work which has been done on the order-disorder problem. The earliest theory of the order-disorder effect was given by Gorsky [14]) in 1928 for alloys of the type AB. He considered the problem as a problem of diffusion and, making some assumptions about the diffusion probabilities, was able to derive a relationship between the long range order, R, and the temperature, T. In 1934 Bragg and Williams [15]) modified the principle used by Gorsky and extended the field of application. In their first paper they used rate processes to derive equations corresponding to Gorsky's equation but later Williams [16]) showed that this was not necessary and that the results could be obtained more rigorously by the methods of statistical mechanics. As the work of Bragg and Williams did much to stimulate research in this subject we give here the essentials of their treatment.

Consider an alloy consisting of N/2 A atoms and N/2 B atoms. (The theory is easily generalised to take into

account the effect of varying the proportions of the constituent atoms.) At the absolute zero the A atoms will lie on certain sites which we call α-sites and the B atoms will lie on β-sites. Let $N_{A\alpha}$, $N_{A\beta}$, $N_{B\alpha}$, $N_{B\beta}$ be the numbers of A and B atoms on the α- and β-sites at a temperature T. We have

$$N_{A\alpha} = N_{B\beta} \quad , \quad N_{A\beta} = N_{B\alpha} \, .$$

We define the long range order parameter, R, by the equation

$$N_{A\alpha} = \frac{N}{4}(1+R).$$

It follows that R=1 corresponds to complete order and R=0 to complete disorder.

The number of ways of achieving a given distribution of the A and B atoms over the lattice sites such that there are $N_{A\alpha}$ A atoms on α-sites, etc., is given by the binomial coefficient

$$W(R) = \frac{(N/2)!}{(N_{A\alpha})!\,(N_{A\beta})!} \cdot \frac{(N/2)!}{(N_{B\alpha})!\,(N_{B\beta})!} \, ,$$

$$= \frac{[(N/2)!]^2}{[\{N(1+R)/4\}!\,\{N(1-R)/4\}!\,]^2} \, .$$

If we now use the Sterling approximation $\ln(x!) \doteq x.\ln(x)-x$ the above expression can be written in the form

$$\ln W(R) = \frac{N}{2}[\, 2\ln 2 - (1+R)\ln(1+R) - (1-R)\ln(1-R)\,] .$$

The entropy of the system, S, in the state characterised

by R is just

$$S = k.\ln\{W(R)\},$$

where k is Boltzmann's constant.

Let the configurational energy of the system be denoted by E(R). Then the free energy of the system is given by

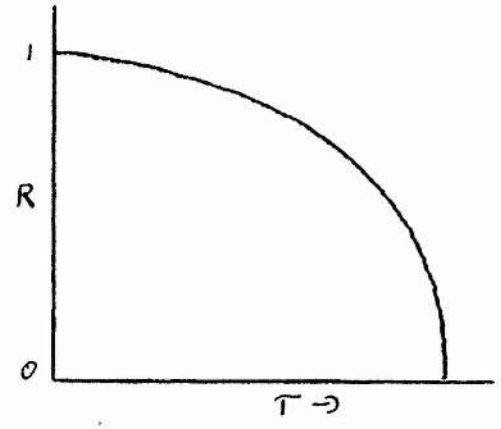
$$F(R) = E(R) - TS$$
$$= E(R) - kT.\ln\{W(R)\},$$

and the dependence of R on T is given by minimising F(R) with respect to R. Before this minimisation can be carried out, however, we have to make some assumption about the ordering energy as a function of R in order to obtain an explicit form for E(R).

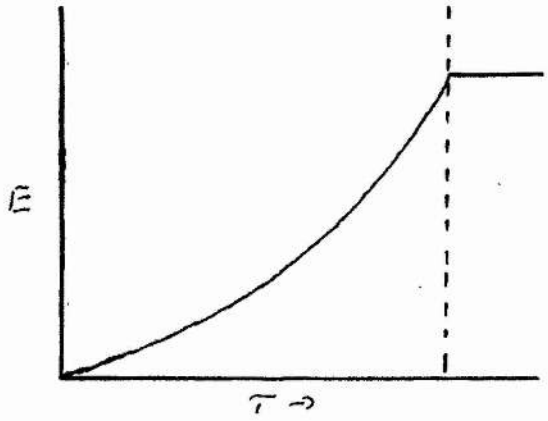
Let V be the energy required to change an A atom on an α-site with a B atom on a β-site. In the state of complete order such an interchange will require a certain definite amount of energy which we call V_o. As the alloy becomes disordered V decreases from V_o until, at the state of complete randomness, V becomes zero. That this should be so follows from the fact that at complete randomness there is no longer any real distinction between the α- and β-sites and therefore there is no energy involved in the interchange. The simplest assumption to make about the dependence of V on R is the one made by Gorsky and by Bragg and Williams, namely

$$V = V_o.R.$$

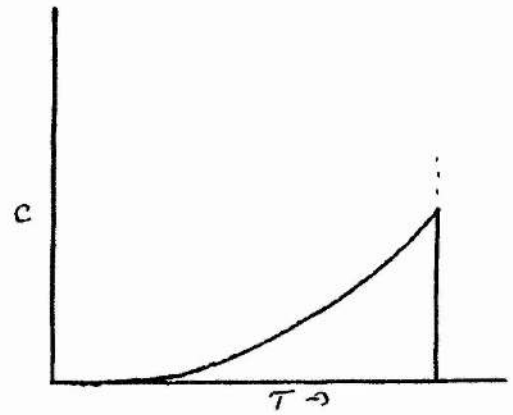
AB case.



a) Long range order versus temperature.



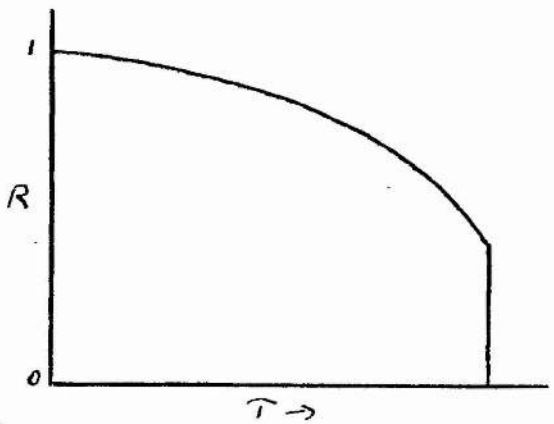
b) Configurational energy versus temperature.

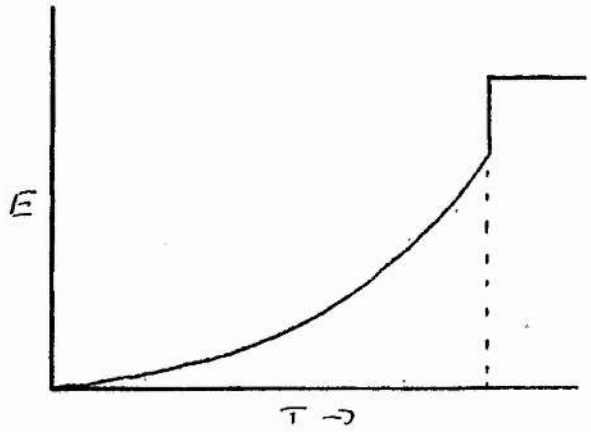


c) Configurational specific heat versus temperature.

Figure 8.

AB_3 case.





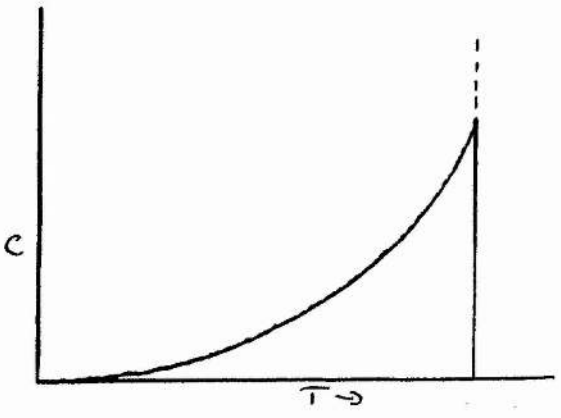


Figure 9.

As the ordering energy between any pair of atoms should depend primarily on the arrangement of their nearest neighbours and only indirectly on the long range order in the crystal, this relationship between V and R is of a rather macroscopic nature. Thus the Bragg-Williams approximation does not take into account the short range order and it is often referred to as the zeroth approximation.

We can now write down an explicit expression for E(R). To increase the order of the system from R to R+dR it is necessary to move a certain number of A atoms from β-sites to α-sites: this number is just $\frac{N}{4}dR$. The corresponding change in the configurational energy of the system is

$$dE = -\frac{N}{4}dR.V$$
$$= -\frac{NV_o}{4}RdR.$$

Integration gives

$$E(R) = -NV_oR^2/8 + \text{constant},$$

and if we choose the zero of energy as the state of complete order we obtain

$$E(R) = NV_o(1-R^2)/8.$$

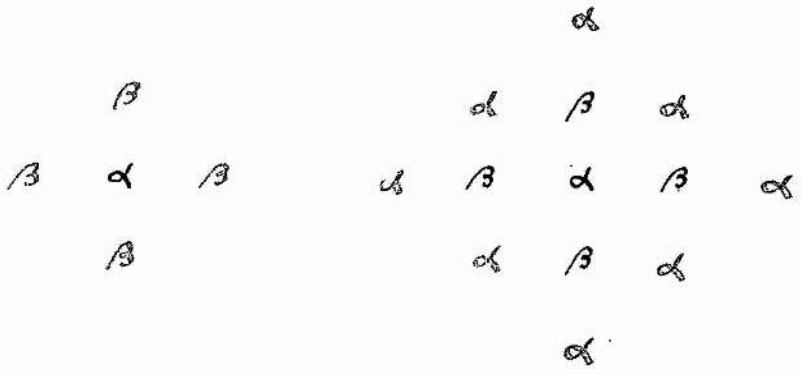
Minimising the free energy with respect to R now gives

$$\partial F/\partial R = NV_oR/4 + (NkT/2)[\ \ln(1+R) - \ln(1-R)\ ] = 0,$$

and hence

$$R = \tanh\{(V_oR)/(4kT)\}.$$

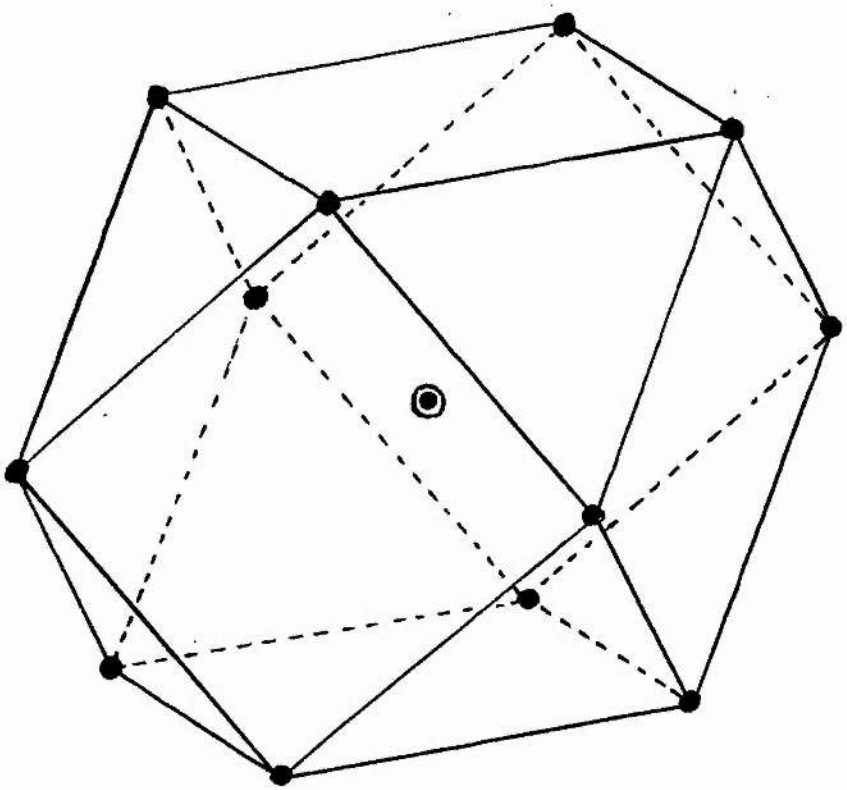
This equation is solved graphically to give R as a function of T. Figure 8a shows the variation of R with T. Above a



a) First approx. b) Second approx.

Black:- interior sites. Red:- boundary sites.

Figure 10.



Central atom ◎ with its twelve nearest neighbours ●.

Figure 11.

certain temperature T_c, which in this case is equal to $\frac{V_o}{4k}$, the stable state of the system is that for which R=0. The configurational energy and configurational specific heat are shown in Figures 8b and 8c. This model gives no contribution to the specific heat above the transition temperature in contrast with the experimental evidence.

Figure 9 shows R, E, and C_v as functions of T in the case of the alloy AB_3.

Bethe [17], in 1935, considered the alloy AB on the basis of a nearest neighbour approximation. He assumed that the mutual potential energy between two atoms decreases rapidly as their separation increases and that only the potential energies between nearest neighbours need be taken into account. Treating the case in which all the nearest neighbours of an α-site are β-sites and vice versa, Bethe selected groups of sites for detailed consideration. His two approximations are represented by the two groups of sites in Figure 10. By considering a given arrangement of atoms on the boundary sites of the group it is possible to calculate the probability that the interior site (or sites) are occupied in a given manner by the A and B atoms. The effect of a state of long range order throughout the lattice on the atoms on the boundary sites is represented by an ordering energy, u. The probability of finding various distributions of atoms over the whole

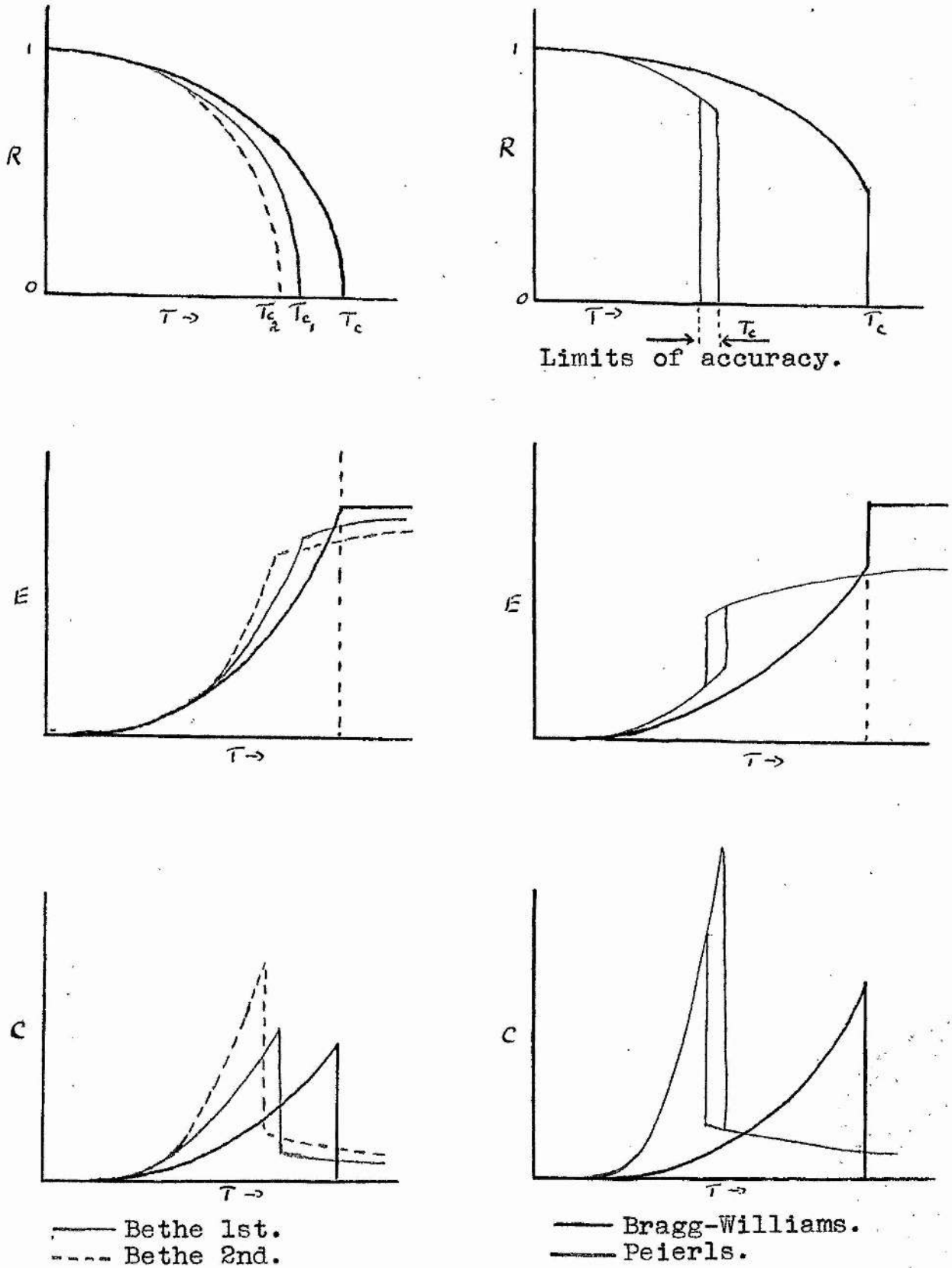

AB case.
AB3 case.
1
R
0
T →
Tc2
Tc1
Tc
Tc
Limits of accuracy.
E
C
—— Bethe 1st.
---- Bethe 2nd.
—— Bragg-Williams.
—— Peierls.

Figure 12.

group can then be evaluated in terms of the unknown u and a consistency relation is used to obtain u as a function of T. Once u has been calculated all the information about the equilibrium state can be found from it.

Peierls applied Bethe's method to the face-centred cubic lattice which is complicated by the fact that the nearest neighbours of some sites are themselves nearest neighbours. In order to obtain results he had to consider a group of twelve sites (see Figure 11) and the working was exceedingly cumbersome [18]. The results of Bethe and of Peierls are compared with those of Bragg and Williams in Figure 12. There is a considerable reduction in T_c and a contribution to the specific heat above T_c.

Also about this time Fowler and Guggenheim [19] developed a method which is now known as the quasi-chemical method. This method has been shown to give the same results, for the simple cubic and body-centred cubic lattices, as those obtained in Bethe's first approximation, but as the quasi-chemical method has a form suited to our requirements we shall treat it here in some more detail.

Consider an alloy of N/2 A atoms and N/2 B atoms arranged on a lattice of N/2 α-sites and N/2 β-sites such that each α-site has z β-sites as its nearest neighbours and vice versa. Let $N_{A\alpha}$, etc., be defined as in the Bragg-Williams approximation: thus we have $N_{A\alpha} = \frac{N}{4}(1+R)$.

Four types of nearest neighbour pair can arise: the numbers of each we denote by

$$\begin{aligned} Q_{\text{A on } \alpha,\ \text{B on } \beta} &= Q_{AB}, \\ Q_{\text{A on } \alpha,\ \text{A on } \beta} &= Q_{AA}, \\ Q_{\text{B on } \alpha,\ \text{B on } \beta} &= Q_{BB}, \\ Q_{\text{B on } \alpha,\ \text{A on } \beta} &= Q_{BA}. \end{aligned}$$

The short range order parameter, σ, is defined by the relation

$$\sigma = (Q_{AB} + Q_{BA} - Q_{AA} - Q_{BB})/Q ,$$

where Q $(= zN/2)$ is the total number of nearest neighbour pairs in the lattice, neglecting surface effects. In terms of R and σ the Q's can be written as follows

$$\begin{aligned} Q_{AA} = Q_{BB} &= \tfrac{Q}{4}(1-\sigma), \\ Q_{AB} &= \tfrac{Q}{4}(1+2R+\sigma), \\ Q_{BA} &= \tfrac{Q}{4}(1-2R+\sigma). \end{aligned}$$

Associated with each nearest neighbour pair will be an interaction energy which we will denote by V_{AA}, V_{BB}, V_{AB}, or V_{BA}. We have $V_{AB} = V_{BA}$. Thus in the nearest neighbour approximation the configurational energy of the system is

$$E = Q_{AA}V_{AA} + Q_{BB}V_{BB} + (Q_{AB} + Q_{BA})V_{AB},$$

and using the above expressions for the Q's we obtain

$$E = \tfrac{Q}{4}(V_{AA} + V_{BB} + 2V_{AB}) - \sigma\tfrac{Q}{4}(V_{AA} + V_{BB} - 2V_{AB}).$$

We note that E does not depend on R but only on σ.

To find the entropy corresponding to given R and σ we have to calculate the number of ways of achieving a given

configuration of the A and B atoms. The fundamental approximation of the quasi-chemical method is that this number, $W(R,\sigma)$, is taken to be equal to, apart from a factor depending on R only, the number of ways of dividing Q pairs into four groups containing Q_{AA}, Q_{BB}, Q_{AB}, and Q_{BA} pairs respectively. This is equivalent to considering the distribution of AA, BB, AB, and BA bonds over the lattice rather than the distribution of A and B atoms, and it is from this fact that the method derives its name.

Thus we have

$$W(R,\sigma) = W'(R).\frac{Q!}{Q_{AA}!Q_{BB}!Q_{AB}!Q_{BA}!}.$$

$W'(R)$ depends on R only and can be evaluated as follows (c.f. Fowler and Guggenheim "Statistical Thermodynamics" page 576.):- For large assemblies we can replace the sum $\sum_{\sigma} W(R,\sigma)$ by the maximum value of $W(R,\sigma)$ with respect to σ. Now $\sum_{\sigma} W(R,\sigma)$ is just the number of ways of obtaining a given value of R, and this is the quantity which we called $W(R)$ in our treatment of the Bragg-Williams approximation on page 15. Thus $\sum_{\sigma} W(R,\sigma) = W(R)$. The value of σ which maximises $W(R,\sigma)$ is easily found to be $\sigma = R^2$. This value of σ gives the values to the Q's which would be found by a simple calculation based on the fact that, on average, each α-site is surrounded by $\frac{z}{2}(1+R)$ B atoms and $\frac{z}{2}(1-R)$ A atoms. Such a procedure ignores the preference for unlike neigh-

bours and is equivalent to the zeroth approximation. We have then

$$W(R) = \sum_{\sigma} W(R,\sigma) \doteq W'(R).\frac{Q!}{(Q_{AA}!Q_{BB}!Q_{AB}!Q_{BA}!)_{\sigma=R^2}} ,$$

and hence

$$W(R,\sigma) = W(R).\frac{(Q_{AA}!Q_{BB}!Q_{AB}!Q_{BA}!)_{\sigma=R^2}}{Q_{AA}!Q_{BB}!Q_{AB}!Q_{BA}!} .$$

Using the Sterling approximation enables us to write the expression for the free energy, $F = E - kT.\ln\{W(R,\sigma)\}$, in the form

$$F = \frac{Q}{4}(V_{AA}+V_{BB}+2V_{AB}) - \sigma\frac{Q}{4}(V_{AA}+V_{BB}-2V_{AB}) - QkT[\ \frac{2}{z}\ln 2 + (1-\frac{1}{z})\{(1+R)\ln(1+R) + (1-R)\ln(1-R)\} - \frac{1}{2}(1-\sigma)\ln(1-\sigma) - \frac{1}{4}(1+2R+\sigma)\ln(1+2R+\sigma) - \frac{1}{4}(1-2R+\sigma)\ln(1-2R+\sigma)\ ].$$

Minimising F with respect to R and σ gives these two quantities as functions of T and of the quantity $J = (V_{AA}+V_{BB}-2V_{AB})$. The minimisation with respect to σ gives at once the basic equation of the quasi-chemical method

$$\frac{Q_{AB}\cdot Q_{BA}}{Q_{AA}\cdot Q_{BB}} = \exp(J/kT).$$

We shall discuss the solution of the quasi-chemical equations more fully when we come to make use of the method in a subsequent chapter.

Kirkwood [20]) pointed out in 1938 that it was possible in principle to evaluate F as a function of R to any desired degree of accuracy. He obtained an expansion in powers of J/kT whose coefficients were polynomials in R - essentially

the semi-invariants of Thiele. After the first few terms, however, the calculations become very laborious.

Other methods have been developed from the point of view of ferromagnetism or anti-ferromagnetism but the transition to substitutional alloys is not difficult to carry out. In 1941 Kramers and Wannier [21]) applied a variational method to the problem and their method has been more recently applied by ter Haar, Martin, and Dempsey to the simple cubic, body-centred cubic, and face-centred cubic lattices both above and below the transition temperatures. The method consists of finding the partition function per spin as the largest eigen-value of a matrix. This matrix approach was suggested independently by Lassettre and Howe and by Montroll in 1941. The exact solution for a two-dimensional square lattice of spins was given by Onsager in 1944. Trefftz in 1950 published some exact results for the three-dimensional cases of interest, these results being obtained by a laborious summation over the various configurations. Much work has been done in this field by, among others, Wakefield, Rushbrooke, Domb, Guggenheim, Yang, and Lee, and we give a comprehensive list of references in the bibliography at the end of this work [22..40]).

All the references [20..40]) are attempts to improve the theory of co-operative phenomena by obtaining a more accurate evaluation of the combinatory factor (or of the

partition function, which amounts to the same thing) than that given, for instance, by the quasi-chemical method. There have been attempts, however, to improve the theory in other directions. After we had started this work we found that in 1938 Eisenschitz had obtained theoretical results which were in reasonable agreement with the experimental values for the specific heat anomaly in β-brass. He made the following assumptions:- 1) The interaction energies between pairs of atoms vary with the square of the change of volume. (In the references above these energies were taken to be constant.) 2) The energy minimum of the average of the Cu-Cu and Zn-Zn energies occurs at a higher value of the volume than does the minimum of the Cu-Zn energy. (This is necessary to give the required anomalous expansion at the transition temperature.) 3) The specimen of β-brass consists of small grains to each of which the theory must be applied individually. The Bragg-Williams method is modified to apply to systems containing only a finite number of atoms and a theoretical estimate allowed Eisenschitz to take a value for this number ($10^4 \sim 10^5$) which gave a good fit with the experimental values above the transition temperature. (This third assumption was necessary in order to obtain a contribution to the specific heat above the transition temperature, such a contribution not being

given by the Bragg-Williams method in its normal form.) Although Eisenschitz's assumption concerning the inter-particle energies is quite similar to the one we make (we assume a quadratic dependence on separation) we consider that the use of the Bragg-Williams approximation is not sufficient. [41]).

More recently Sarolea [42]) has considered the effects of lattice vibrations and volume changes on the order-disorder transition. The volume change effects are introduced in a way quite different from that appearing in our calculations and our conclusions are somewhat different. Booth and Rowlinson [43]) have given a treatment such that the effect of the lattice vibrations can be calculated independently of the form of the combinatory factor, and they show that this effect is considerable, at anyrate for the case of β-brass. Hovi [44]) has obtained expressions for the thermal expansion of a substitutional alloy using Kirkwood's method of approximation. His equations suggest that there is a discontinuity in the thermal expansion at the transition temperature.

II

THE LINEAR LATTICE.

1 Although a linear lattice does not exhibit an order-disorder transition it provides a useful and simple introduction to the study of the volume change effect and we believe that it shows the main features of this effect.

We consider first a linear chain consisting of N/2 A atoms and N/2 B atoms. In the first, rather trivial, model we assume that an A-A pair, an A-B pair, and a B-B pair have associated with them the constant separations r_A, r_o, and r_B and the constant energies V_{AA}, V_{AB}, and V_{BB} respectively. We assume throughout this work that only nearest neighbour interactions need be taken into account. It is convenient to define the quantity V by the equation

$$V = \frac{1}{2}(V_{AA} + V_{BB}) - V_{AB}$$

and we take $V > 0$ in order to obtain the ordered structure ABABAB... at the absolute zero.

Let Q_{AA}, Q_{BB} and Q_{AB} be the number of nearest neighbour pairs which are A-A, B-B, and A-B pairs respectively. The configurational energy of the system is then given by

$$E = Q_{AA}V_{AA} + Q_{BB}V_{BB} + Q_{AB}V_{AB}.$$

From symmetry considerations it follows that $Q_{AA} = Q_{BB}$, and since the total number of nearest neighbour pairs is

equal to N we have $Q_{AA} = Q_{BB} = \frac{1}{2}(N - Q_{AB})$, and hence

$$E = V(N - Q_{AB}). \qquad 2.1$$

The length of the linear chain is given by the relation

$$L = Q_{AA}r_A + Q_{BB}r_B + Q_{AB}r_o$$

$$= N(r_A+r_B)/2 - Q_{AB}\{(r_A+r_B)/2 - r_o\}.$$

Substituting the value of Q_{AB} given by equation 2.1 gives

$$L = Nr_o + \frac{E}{V}\{(r_A+r_B)/2 - r_o\}. \qquad 2.2$$

In the case of the linear chain with composition AB the dependence of E on temperature has been found to be (c.f. Kramers and Wannier 1941)

$$E = \frac{1}{2}NV(1 - \tanh X), \qquad X = V/2kT.$$

Combining this result with equation 2.2 gives us the length of the chain as a function of temperature.

$$L = Nr_o + \frac{N}{2}\{(r_A+r_B)/2 - r_o\}(1 - \tanh X). \qquad 2.3$$

The rate of change of length with temperature, which in this case is proportional to the specific heat, is

$$dL/dT = \frac{Nk}{V}\{(r_A+r_B)/2 - r_o\}(X/\cosh X)^2 \propto dE/dT.$$

Since most substances expand when heated we wish to have

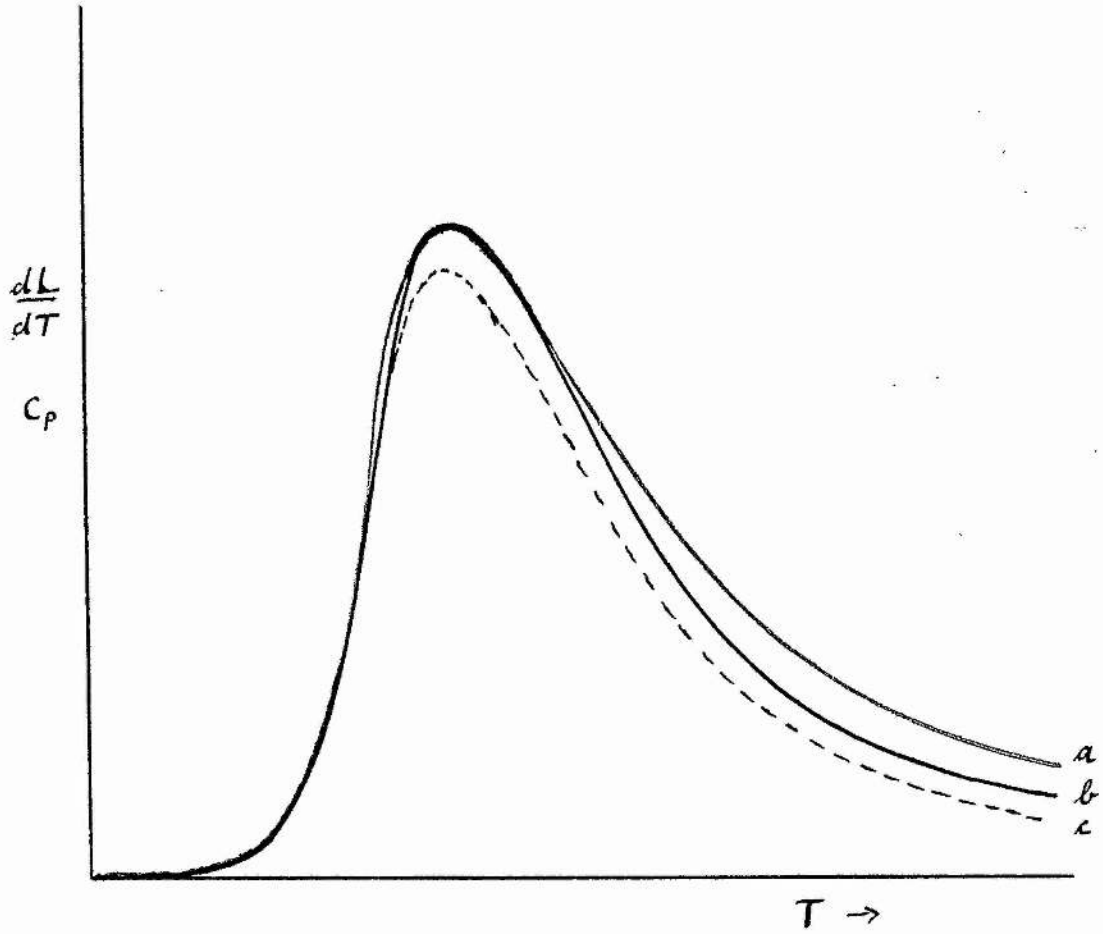


Figure 13.

$dL/dT > 0$ and thus we must have $(r_A + r_B)/2 > r_o$. In this case the variation of dL/dT with temperature is as shown in Figure 13a.

This model, containing three different lattice spacings r_A, r_B, and r_o, cannot be applied to the case of a square net or of a three-dimensional lattice and we therefore consider the following modification. We assume that there is a uniform spacing, r, between neighbouring atoms in the chain and that the energies V_{AA}, V_{BB}, and V_{AB} associated with the three types of pair are dependent on the value of r. The dependence of r on T will follow from the thermodynamical condition of minimum free energy.

As before we wish to consider the case where the arrangement of the atoms at the absolute zero is ABABAB... Let Q_{YZ} be the number of pairs which consist of a Y atom on one site and a Z atom on the adjacent right hand site. As an illustration the arrangement ABBAABAABB corresponds to the values $Q_{AB} = 3$, $Q_{BA} = 2$, $Q_{AA} = 2$, $Q_{BB} = 2$. In the case where there are equal numbers of A and B atoms, these numbers being large enough to neglect end effects, the following relations hold (c.f. ter Haar, 1954, XI1,4 [45]))

$$Q_{AA} = Q_{BB} \quad , \qquad Q_{AB} = Q_{BA} \, ,$$

$$Q_{AA} = \frac{N}{2} - Q_{AB} \, .$$

The number of ways of obtaining a given distribution,

Q_{AA}, Q_{BB}, Q_{AB}, Q_{BA}, is the compound probability

$$W = \frac{N!}{Q_{AA}!\,Q_{BB}!\,Q_{AB}!\,Q_{BA}!},$$

and the entropy of the chain is

$$S = k.\ln W$$

$$= k[\, N\ln N - 2(N/2 - Q_{AB})\ln(N/2 - Q_{AB}) - 2Q_{AB}\ln Q_{AB}\,].$$

The energy of the chain is

$$E = Q_{AA}V_{AA} + Q_{BB}V_{BB} + Q_{AB}V_{AB} + Q_{BA}V_{BA}$$

$$= \frac{N}{2}(V_{AA} + V_{BB}) - Q_{AB}(V_{AA} + V_{BB} - 2V_{AB}),$$

and for the free energy we obtain

$$F = E - TS$$

$$= \frac{N}{2}(V_{AA} + V_{BB}) - Q_{AB}(V_{AA} + V_{BB} - 2V_{AB}) - kT[\, N\ln N -$$

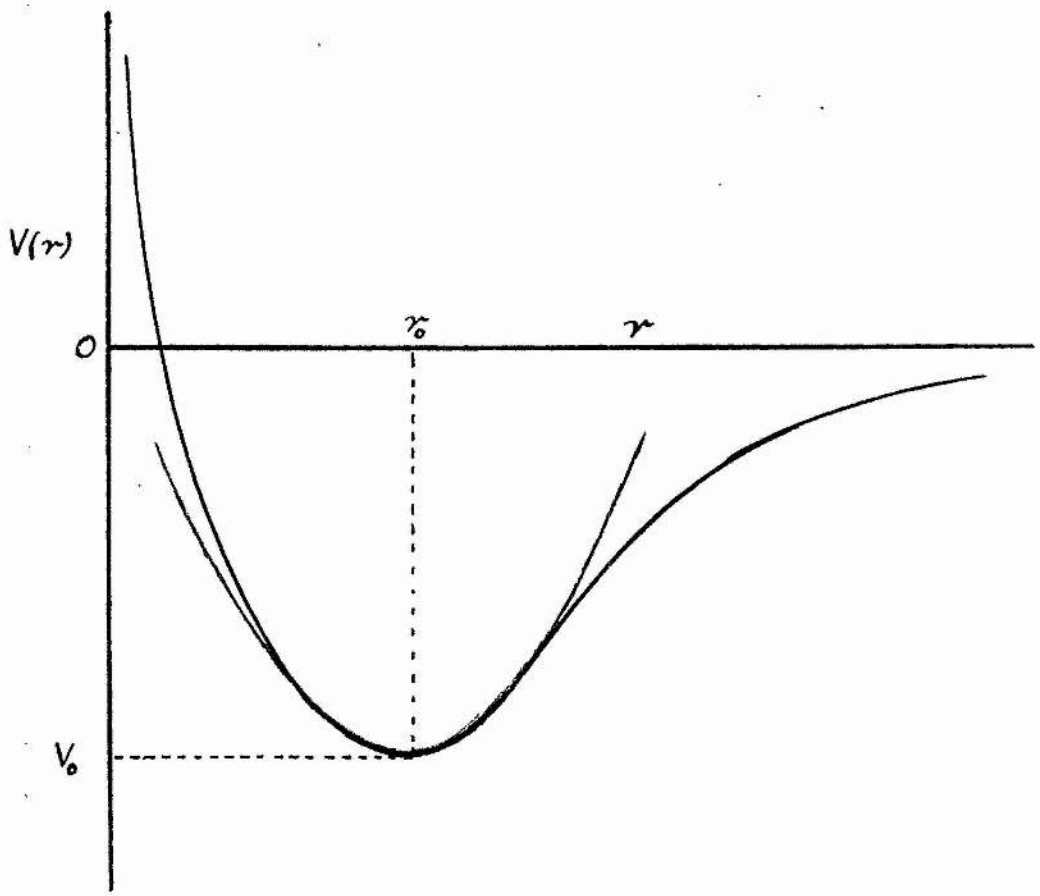
$$2(N/2 - Q_{AB})\ln(N/2 - Q_{AB}) - 2Q_{AB}\ln Q_{AB}\,].$$

Minimising F with respect to Q_{AB} and r gives

$$\frac{\partial F}{\partial Q_{AB}} = 0 = -(V_{AA} + V_{BB} - 2V_{AB}) - 2kT[\ln(N/2 - Q_{AB}) - \ln Q_{AB}],$$

$$\frac{\partial F}{\partial r} = 0 = \frac{N}{2}.\frac{d}{dr}(V_{AA} + V_{BB}) - Q_{AB}.\frac{d}{dr}(V_{AA} + V_{BB} - 2V_{AB}).$$

From these two equations we have finally



—— *Morse potential*

$$V(r) = \frac{D}{4} e^{-a(r-r_0)} \left\{ e^{-a(r-r_0)} - 2 \right\}$$

where $D > 0$, $a > 0$.

—— *Parabolic potential*

$$V(r) = V_0 + D'(r-r_0)^2$$

where $V_0 \approx -\frac{D}{4}$, $D' \approx \frac{D}{4} a^2$.

Figure 14.

$$V_{AA}+V_{BB}-2V_{AB} = -2kT.\ln\left[\left\{\frac{d}{dr}(-2V_{AB})\right\}/\left\{\frac{d}{dr}(V_{AA}+V_{BB})\right\}\right] \quad 2.4$$

and this equation gives r as a function of T when the dependence of the V's on r is known. We assume the following form for the V_{YZ}:

$$V_{YZ} = V_o + D(r - r_{YZ})^2 .$$

This variation of the interparticle energy with r was chosen as representing reasonably well the lower part of the potential energy function of an atomic pair such as is given for instance by a Morse potential, Figure 14. In a research note in the Proceedings of the Physical Society, A, LXVII, 1954 we made the following simplifying assumptions

$$V_{AA} = V_{BB} = V_o' + D'(r - r_1)^2$$

$$V_{AB} = V_{BA} = V_o + D(r - r_2)^2 .$$

r_1 was taken to be greater than r_2 corresponding to the fact that ordering is known experimentally to be accompanied by a diminution of volume, and we put $D' = D$ corresponding to the fact that the frequencies in most diatomic systems are of the same order of magnitude. We stated that $V_o'-V_o$ had to be greater than $D(r_1 - r_2)^2$ in order to obtain the required distribution ABABABAB... at the absolute zero but this is too stringent a condition

as can be seen from the following considerations. It is convenient to introduce the quantity m defined by

$$r = r_2 + m(r_1 - r_2).$$

Thus in terms of the parameter m we have

$$V_{AA} = V'_o + D(r_1 - r_2)^2(1-m)^2$$

$$V_{AB} = V_o + D(r_1 - r_2)^2 m^2 \quad ,$$

and equation 2.4 becomes

$$V'_o - V_o + D(r_1 - r_2)^2(1-2m) = kT.\ln[\,(1-m)/m\,].$$

Put $V'_o - V_o = \theta D(r_1 - r_2)^2$ and let $(kT)/\{D(r_1 - r_2)^2\} = x$.

$$x = \frac{\theta + 1 - 2m}{\ln(\frac{1-m}{m})} \qquad 2.5$$

We see from equation 2.5 that as the temperature is raised from zero to infinity (x going from 0 to ∞) m increases from the value zero and approaches the value 1/2 asymptotically, in agreement with the fact that the state of greatest disorder has as many A-A or B-B pairs as it has A-B or B-A pairs. The quantity $\theta + 1 - 2m$ must be positive: its least value is equal to θ when $m = 1/2$. Thus we must have $\theta > 0$ and hence the condition that the quantity $V'_o - V_o$ must satisfy is $V'_o - V_o > 0$.

We have used equation 2.5 to calculate m as a function

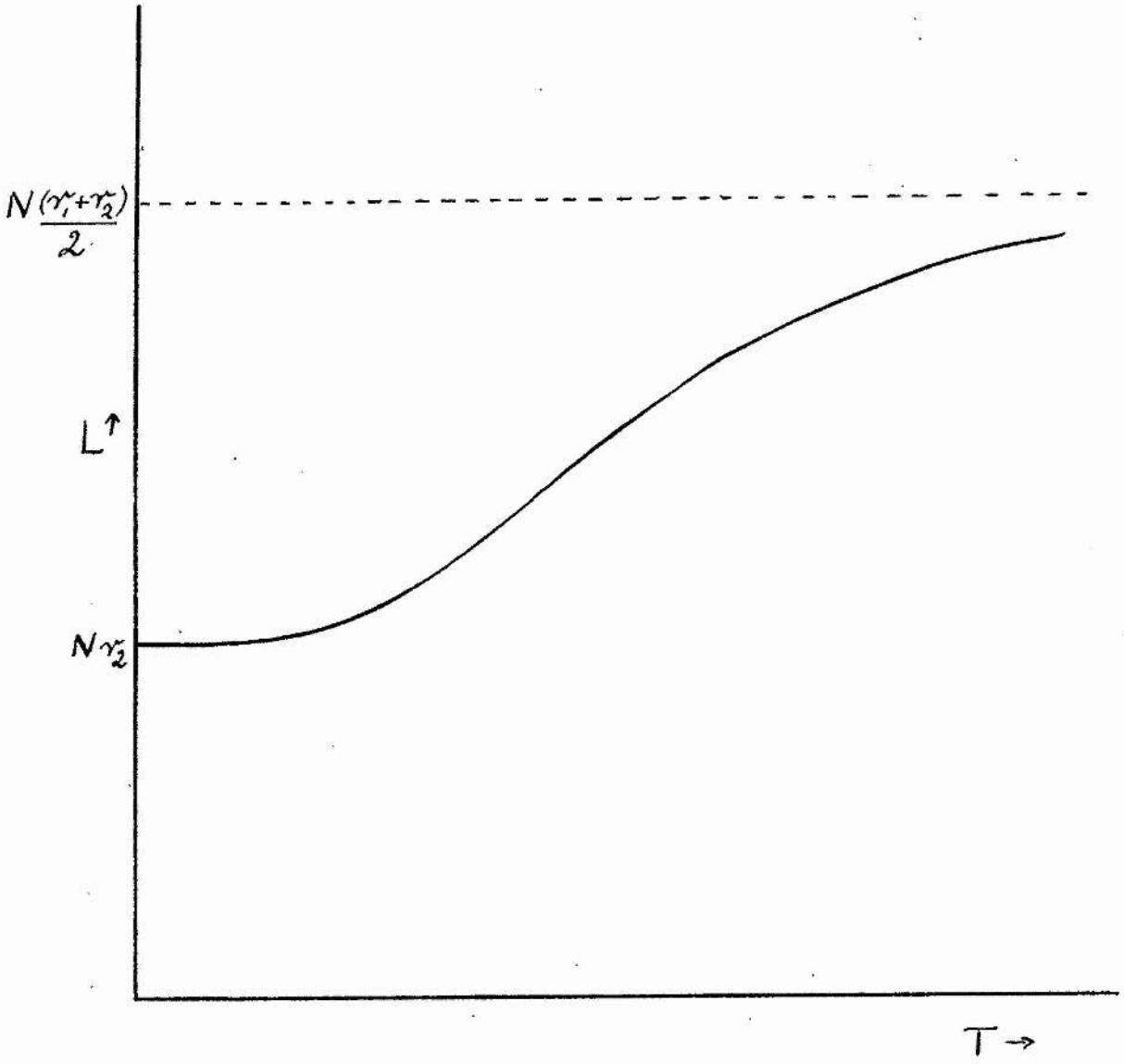


Figure 15.

of x for the case $\theta = 2$. With this value of θ and values of D, r_1, r_2 to be expected from data about potential energy functions, $V_o' - V_o$ turns out to be (at most) of the order of ·1 electron volts, which seems a reasonable value (c.f. Nix and Shockley 1938.[46]).

The length of the chain is given by $L = Nr_2 + N(r_1 - r_2)m$ and its variation with temperature is shown in Figure 15. The rate of change of L with temperature is given by the equation

$$dL/dT = N(r_1 - r_2)(dm/dT) \propto dm/dx,$$

and the dependence of dL/dT on T is shown in Figure 13b.

The specific heat at constant pressure, C_p, is found from the relation $C_p = T(dS/dT)_p$ to be

$$C_p = \tfrac{1}{2}Nk(3-2m)(dm/dx).$$

The variation of C_p with T is shown also on Figure 13c. It is seen from a comparison of curves a and b of Figure 13 that there is not a great deal of difference between the two models which we have considered. (We should of course state here that, to obtain the best comparison of the two curves, we have multiplied the ordinate 1/X of the first model by 1·536 and the quantity $(X/\cosh X)^2$ by ·412. This ensures that the maxima of the two curves have the same value, and occur at the same value of the ordinate.)

Although the specific heat is no longer proportional to dL/dT as was the case in our first model the two curves 13b and 13c are still very similar and the maxima of C_p and dL/dT occur at approximately the same temperature. We therefore expect a similar behaviour in the case of a two- or three-dimensional substitutional alloy and a discontinuity in the expansion coefficient corresponding to the discontinuity in the specific heat.

2 It is of some importance to investigate the effects of the simplifying assumptions which we have made. Firstly we note that varying the parameter θ will not cause any significant change provided it does not approach the value zero too closely. The main effect of varying θ is to change the temperature scale. Reducing θ reduces the value of x appropriate to a given value of m, that is to say that m increases more rapidly with temperature the smaller θ is. This is as we should expect since a small value of θ implies a small value of $V_o' - V_o$ and the smaller this quantity is the easier it is to form A-A and B-B pairs from the original A-B pairs.

The specific heat is given by $C_p \propto (\theta+1-2m)(dm/dx)$. For the larger values of θ, C_p becomes more nearly proportional to dm/dx, and even for the smaller values of θ the presence of the term 1 in the factor $(\theta+1-2m)$ is sufficient to ensure a reasonable degree of proportionality in the

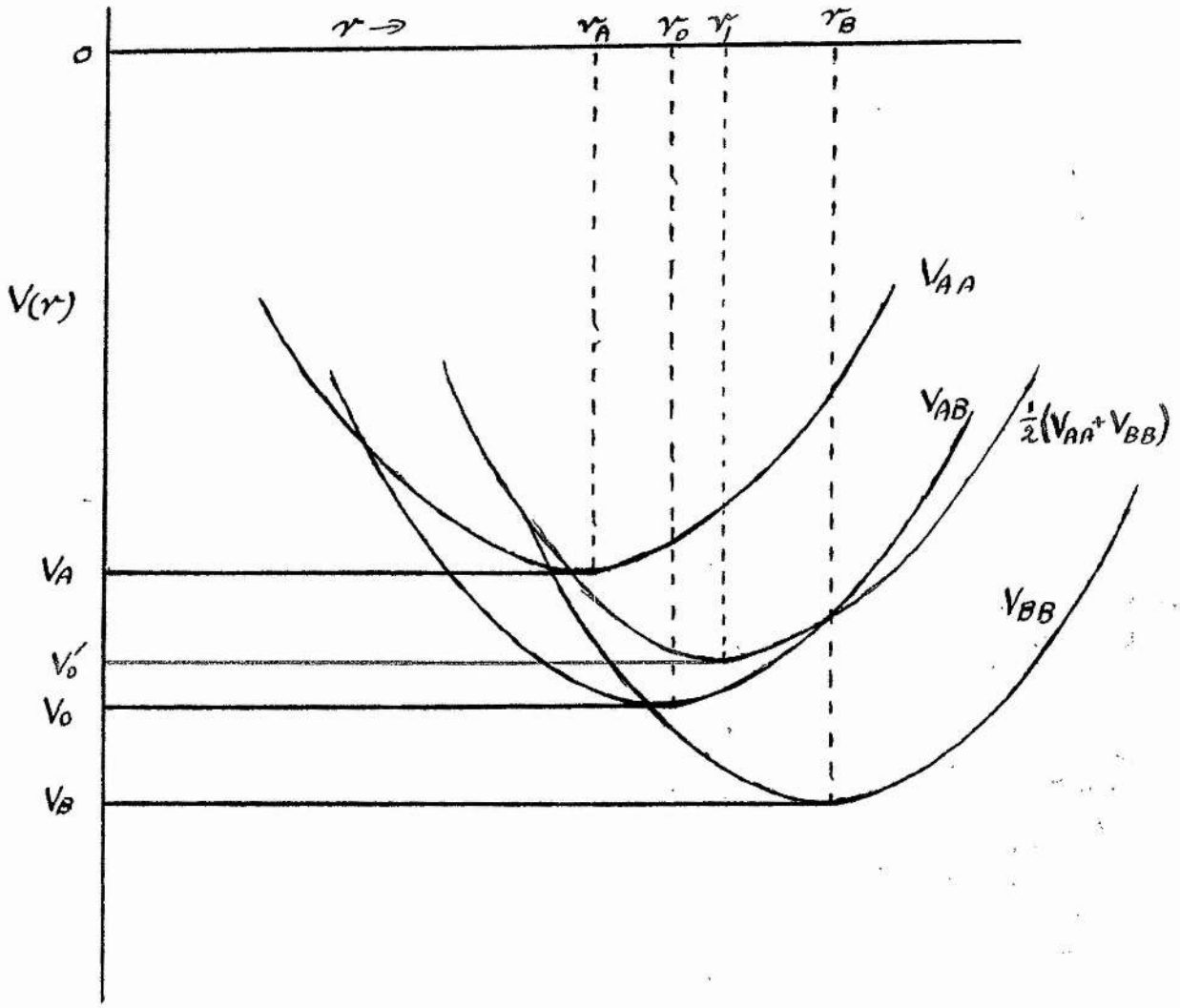


Figure 16.

region of interest, namely near the maximum, since the maximum of dm/dx occurs for small values of m.

The simplifying assumption $V_{AA} = V_{BB}$ involves no loss in generality. These two quantities occur only in the combination $V_{AA} + V_{BB}$ and if we take

$$V_{AA} = V_A + D(r - r_A)^2 ,$$

$$V_{BB} = V_B + D(r - r_B)^2 ,$$

we find

$$(V_{AA}+V_{BB})/2 = (V_A+V_B)/2 + D(r_A-r_B)^2/4 + D\{r-(r_A+r_B)/2\}^2 ,$$

which is a parabolic potential energy function with minimum value equal to $(V_A+V_B)/2 + D(r_A-r_B)^2/4$, occurring at the distance $(r_A+r_B)/2$. Thus we may consider V_o' and r_1 as representing these two quantities respectively. One would expect intuitively that the function V_{AB} should lie between the functions V_{AA} and V_{BB} and the condition $V_o'-V_o > 0$ is a restriction on its position. Hence, if the ordered state ABABAB... is to be the equilibrium state at the absolute zero, the minimum of the AB potential energy function must lie below the minimum of the average of the AA and BB potential energy functions. Figure 16 shows one possible arrangement which fulfils this requirement.

The situation is slightly more complicated in the case

where $D_A \neq D_B \neq D$, although we can still replace the quantity $(V_{AA}+V_{BB})/2$ by a parabolic potential energy function $V_o' + D'(r - r_1)^2$. The following equations are easily verified.

$$V_o' = (V_A+V_B)/2 + D_A.D_B.(r_A-r_B)^2/\{2(D_A+D_B)\},$$

$$D' = (D_A+D_B)/2,$$

$$r_1 = (D_A.r_A + D_B.r_B)/(D_A+D_B).$$

If now we put $D'/D = \phi$, $(V_o'-V_o)/\{D(r_1-r_2)^2\} = \theta$, and $r = r_2 + m(r_1-r_2)$, we find from equation 2.4

$$x = \frac{\theta + \phi - 2\phi m + (\phi-1)m^2}{\ln\{\phi(1-m)/m\}}. \qquad 2.6$$

(We note that equation 2.5 is a special case of equation 2.6 obtained by putting $\phi = 1$.) One would expect ϕ to be not very different from unity so that the term $(\phi-1)m^2$ in the numerator will be much smaller than the other terms and since, in the case of the linear lattice, there is no transition which might be affected by the presence of this term we did not think it worthwhile to carry out numerical calculations for values of ϕ other than unity. Equation 2.6, however, gives us the conditions which the quantities θ and ϕ must obey in order that the system should show the required variation with temperature and as we shall need these conditions in subsequent chapters we derive them here.

Since the equilibrium state at the absolute zero is to be the arrangement ABABAB... we have at once $\theta > 0$. The interparticle spacing in this state is r_2 and so $m = 0$ at $T = 0$. As the temperature is raised from 0 to ∞, m increases from 0 to the value which makes the divisor $\ln\{\phi(1-m)/m\}$ equal to zero, that is, to the value $\phi/(1+\phi)$, the interparticle spacing being then equal to $(\phi r_1 + r_2)/(1+\phi)$. For all values of m between 0 and $\phi/(1+\phi)$ the numerator of equation 2.6 must remain positive, since x is proportional to T and $\ln\{\phi(1-m)/m\}$ is positive, and since it decreases as m increases its least value will occur at the maximum value of m, that is, when $m = \phi/(1+\phi)$. It follows, therefore, that if the system is to change from the state ABABAB... at the absolute zero to a state in which there are as many A-A and B-B pairs as there are A-B pairs at the highest temperatures we must have

$$\theta + \{\phi(1-\phi)\}/\{(1+\phi)^2\} > 0. \qquad 2.7$$

It is easily verified that this is just the condition that $V_o' + D'(r-r_1)^2 > V_o + D(r-r_2)^2$, or $(V_{AA}+V_{BB})/2 > V_{AB}$ for all values of r from r_2 to $(\phi r_1 + r_2)/(1+\phi)$ inclusive. Since $\theta > 0$ the above inequality is automatically satisfied for values of ϕ less than unity. For the values of ϕ which are greater than unity the above condition is a more stringent one than $\theta > 0$. Figure 17 shows the cases that

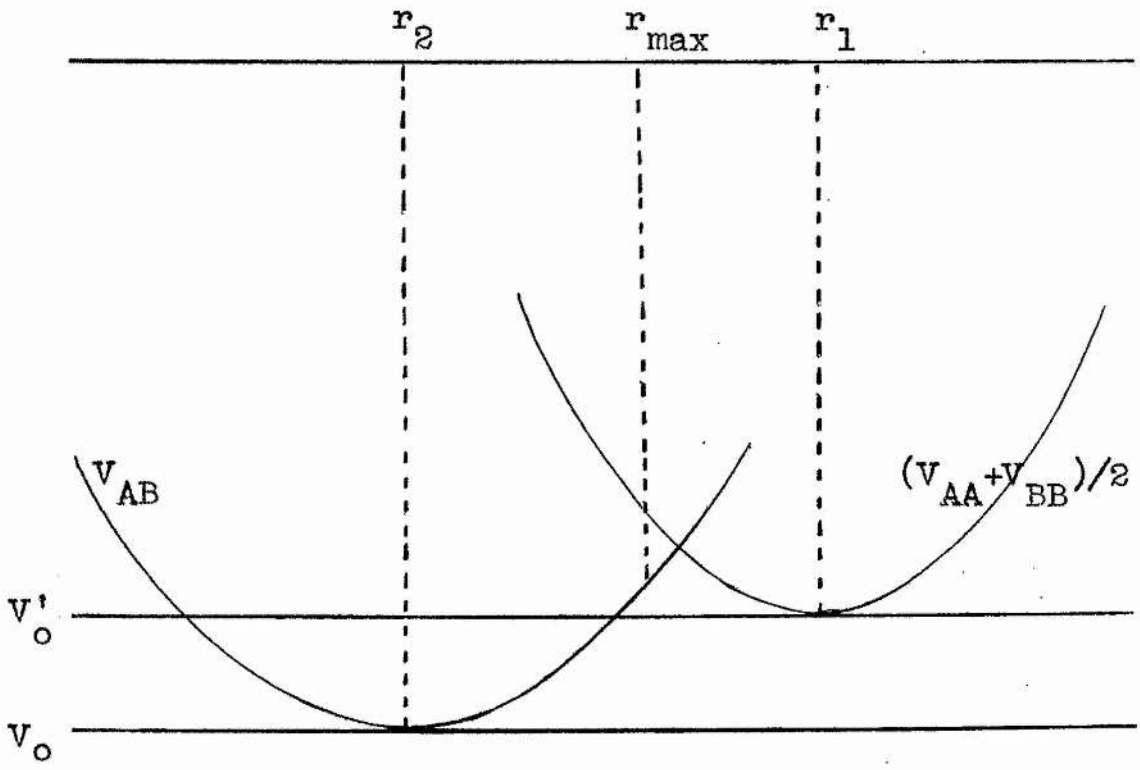


Figure 17a.

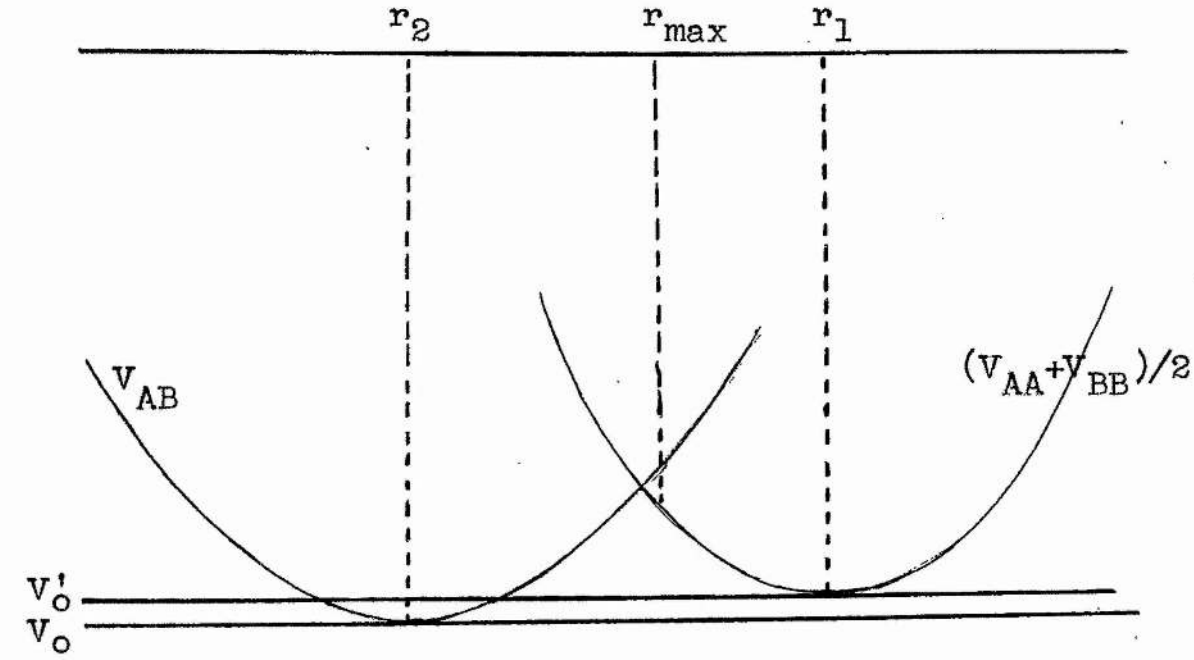


Figure 17b.

can arise when $\emptyset > 1$. In Figure 17a the potential energy curves are so placed that the condition 2.7 is satisfied, and in this case r_{max} ($= \{\emptyset r_1 + r_2\}/\{1+\emptyset\}$) lies to the left of the point of intersection of the two curves. It is clear from the figure that in this case A-B pairs are energetically more favourable than A-A or B-B pairs for all values of the interparticle spacing between r_2 and r_{max}. In Figure 17b on the other hand the condition 2.7 is not satisfied and r_{max} lies to the right of the point of intersection of the two potential energy curves. In this case there are values of r for which A-A and B-B pairs are energetically more favourable than A-B pairs leading to a possible phase separation. In this case, of course, we should have to define our parameter, m, somewhat differently in order to obtain the complete description of the variation of the interparticle spacing with the temperature. The following work, however, will be concerned only with systems in which unlike pairs are energetically favoured at all values of the temperature.

III

THE SIMPLE CUBIC AND BODY-CENTRED CUBIC LATTICES

1 In this chapter we consider an assembly of N/2 A atoms and N/2 B atoms occupying the sites of a simple cubic or body-centred cubic lattice. We assume that the equilibrium state at the absolute zero is that in which all the nearest neighbours of the A atoms are B atoms and vice versa and we use this arrangement to label the sites of the lattice. Thus we have an arrangement of N/2 α-sites and N/2 β-sites such that each α-site has z (= 6 or 8) β-sites as its nearest neighbours and vice versa. We define the long range order, R, and the short range order, σ, as in chapter I (pages 19 and 20) and we use the quasi-chemical approximation (as described in pages 19 to 22) to obtain the free energy of the system as a function of R and σ. If we neglect the effect of the lattice vibrations and consider only the contributions to the energy arising from the nearest neighbour interactions we find for the energy, E, of the system the expression (see page 20)

$$E = (Nz/8)\{(V_{AA} + V_{BB} + 2V_{AB}) - \sigma(V_{AA} + V_{BB} - 2V_{AB})\}.$$

The first approximation is to assume that the quantities V_{AA}, V_{BB}, V_{AB}, the nearest neighbour potential energies associated with A-A, B-B and A-B pairs respectively, are constant and with this assumption it has been shown that

the quasi-chemical approximation gives a second order transition. We wish to investigate what changes, if any, occur in the transition temperature and in the nature of the transition when we let V_{AA}, V_{BB} and V_{AB} depend on the lattice spacing and hence on the temperature.

We assume, as in the previous chapter, that the dependence of the interparticle potential energies on the lattice spacing, r, is sufficiently well represented in the region of interest by the expressions

$$V_{AA} = V_A + D_A(r - r_A)^2, \qquad V_{BB} = V_B + D_B(r - r_B)^2,$$

$$V_{AB} = V_o + D(r - r_o)^2.$$

Since the system with which we are concerned contains equal numbers of A and B atoms the quantities V_{AA} and V_{BB} occur only in the combination $V_{AA} + V_{BB}$ and hence we may put, without any loss in generality,

$$V_{AA} = V_{BB} = V_o' + D'(r - r_1)^2.$$

In order to obtain the required equilibrium state at the absolute zero we must have $V_o' > V_o$ and as most substances expand when heated we take $r_1 > r_o$. We define parameters m, Θ and ϕ by the relations

$$r = r_o + m(r_1 - r_o), \quad V_o' - V_o = \Theta D(r_1 - r_o)^2, \quad \phi = D'/D,$$

and we find the following expression for E:

$$E = (Nz/4)(V_o'+V_o)$$

$$+ (Nz/4)D(r_1-r_o)^2[\phi-2\phi m+(\phi+1)m^2 - \sigma\{\theta+\phi-2\phi m+(\phi-1)m^2\}].$$

Inserting this value of E in the expression for the free energy, F, derived by the quasi-chemical method in chapter I (page 22) gives us the free energy of the system as a function of R, σ and m and hence enables us to calculate R, σ and m (i.e. r) as functions of the temperature, T. It is convenient to use the variable $x = kT/\{2D(r_1-r_o)^2\}$ rather than just T, and to use F' defined by

$$F' = \{F - (Nz/4)(V_o'+V_o)\}/NzD(r_1-r_o)^2$$

in place of F. Thus after simplification we find

$$F' = (1/4)[\phi-2\phi m+(\phi+1)m^2 - \sigma\{\theta+\phi-2\phi m+(\phi-1)m^2\}]$$

$$- x[(2/z)\ln(2) + \{(z-1)/z\}\{(1+R)\ln(1+R) + (1-R)\ln(1-R)\}$$

$$-(1/2)(1-\sigma)\ln(1-\sigma) - (1/4)(1+2R+\sigma)\ln(1+2R+\sigma)$$

$$- (1/4)(1-2R+\sigma)\ln(1-2R+\sigma)]. \qquad 3.1$$

We now obtain the equilibrium values of R, σ and m as functions of the temperature by minimising F' with respect to these three parameters. Strictly speaking we should not equate $\partial F'/\partial m$ to zero since $\partial F'/\partial m = (\partial F'/\partial v)(dv/dm)$ where v is the volume of the system. Now $\partial F'/\partial v = - p$ where p is the pressure on the system. In this case p is just the

atmospheric pressure and from the present point of view this is negligible compared to the other terms involved. Thus we have

$$\partial F'/\partial R = 0 = -x[\{(z-1)/z\}\ln\{(1+R)/(1-R)\} - (1/2)\ln\{(1+2R+\sigma)/(1-2R+\sigma)\}] \qquad 3.2$$

$$\partial F'/\partial \sigma = 0 = -(1/4)\{\theta+\phi-2\phi m+(\phi-1)m^2\} - (x/4)\ln\{(1-\sigma)^2/(1+2R+\sigma)(1-2R+\sigma)\} \qquad 3.3$$

$$\partial F'/\partial m = 0 = -(1/4)[-2\phi+2(\phi+1)m - \sigma\{-2\phi+2(\phi-1)m\}] \qquad 3.4$$

It is not practical to solve these three equations directly to obtain R, σ and m as functions of x. It is most convenient to take R as the independent variable and to calculate σ, m and x as functions of R. Equation 3.2 gives

$$\sigma = 2R(Z+1)/(Z-1) - 1, \qquad Z = \{(1+R)/(1-R)\}^{2(z-1)/z}. \qquad 3.5$$

Equation 3.4 gives

$$m = \phi(1-\sigma)/\{1+\sigma+\phi(1-\sigma)\}. \qquad 3.6$$

Substituting this value of m into equation 3.3 gives

$$x = \frac{\theta + \phi\{(1+\sigma)^2 - \phi(1-\sigma)^2\}/\{1+\sigma+\phi(1-\sigma)\}^2}{\ln\{(1+2R+\sigma)(1-2R+\sigma)/(1-\sigma)^2\}}. \qquad 3.7$$

If we had not included the volume dependence of the inter-

particle potential energies we would have obtained instead of equation 3.7 the expression

$$x = \theta/\ln\{(1+2R+\sigma)(1-2R+\sigma)/(1-\sigma)^2\}$$

the solution of which gives the curves of Figure 3a.

We used equation 3.5 to calculate σ as a function of R for the two cases z = 6 and z = 8, letting R range from 0 to 1 in steps of .01, and then evaluated the quantity

$$M = \ln\{(1+2R+\sigma)(1-2R+\sigma)/(1-\sigma)^2\}$$

(and also L = 1/M).

2 The case z = 6.

As R decreases from 1 to 0 σ decreases from 1 to .2 and M decreases from ∞ to ln(2.25). At temperatures above the transition temperature the long range order is always zero and the state of the system is characterised by the value of the short range order. Hence, for temperatures above the transition temperature, we use σ as the independent variable for the purposes of calculation and the quantity M becomes

$$M = (2)\ln\{(1+\sigma)/(1-\sigma)\} \qquad .2 \geqslant \sigma \geqslant 0.$$

In this range M decreases from ln(2.25) as σ decreases from .2 and tends to zero as σ tends to zero. M is always positive and, since x must always be positive, we must

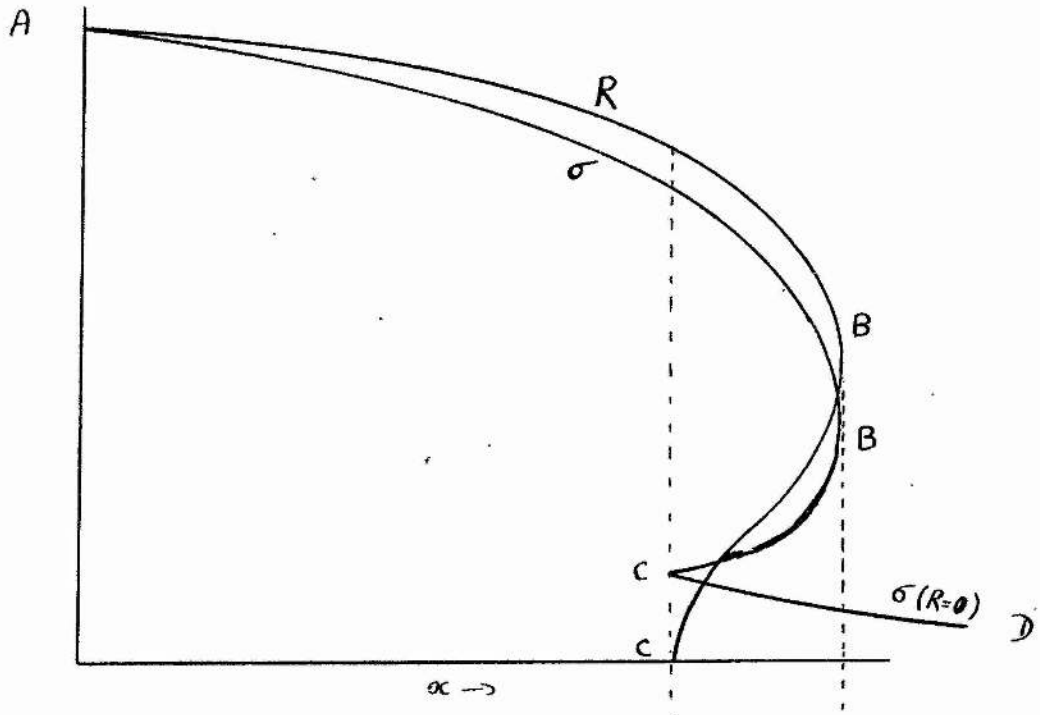


Figure 18a.

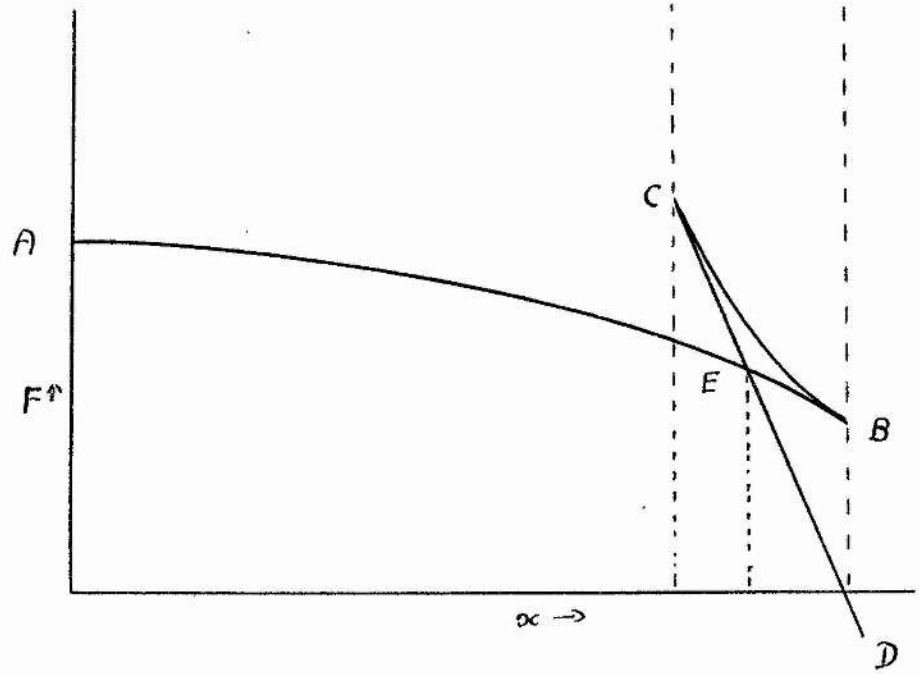


Figure 18b.

have the condition

$$\theta + \{\phi(1-\phi)\}/\{(1+\phi)^2\} > 0.$$

This is just the condition which was found in chapter II (equation 2.7), and discussed therein. We evaluated x as a function of R in the range $1 \geqslant R \geqslant 0$, and as a function of σ in the range $R = 0$, $.2 \geqslant \sigma \geqslant 0$ for a series of values of θ and ϕ which satisfied this condition. θ took the values 0, .1, .5, 1, 1.1, 1.5, 2, 2.5, and ϕ took the values .5, .75, 1, 1.25, 1.5, 2. We found that for most pairs of values of θ and ϕ the variation of R with x was no longer of the form shown in Figure 3a but had changed to the form shown in Figure 18a. This form has a range of values of x for which there are two values of R (other than $R = 0$) satisfying $\partial F'/\partial R = 0$.

If we use equations 3.5, 3.6 and 3.7 we can write the free energy in the convenient form

$$F' = \theta/4 + (\phi/2)(1+\sigma)^2/\{1+\sigma+\phi(1-\sigma)\}^2$$

$$- x[(1/3)\ln(2) + (5/6)\ln(1-R^2) - \ln(1-\sigma)]. \qquad 3.8$$

For temperatures at which there is no long-range order present we would have, instead of equation 3.8,

$$F' = \theta/4 + (\phi/2)(1+\sigma)^2/\{1+\sigma+\phi(1-\sigma)\}^2$$

$$- x[(1/3)\ln(2) - \ln(1-\sigma)]. \qquad 3.9$$

We evaluated the free energy as a function of x using equation 3.8 for the range $1 \geqslant R \geqslant 0$ and using equation 3.9 for the range $R = 0$, $.2 \geqslant \sigma \geqslant 0$. A typical variation of F' with x is shown in Figure 18b. The parts of the free energy curve marked AB and BC are obtained from equation 3.8 and correspond to the regions AB and BC of the graphs of R and σ versus x, and the part CD is obtained from equation 3.9 and corresponds to the region CD of the graph of σ versus x. Figure 18b shows that for values of x less than the value corresponding to the point E the state of lowest free energy is that for which R lies between 1 and R_E, and for higher values of x the state of lowest free energy is that for which $R = 0$. Thus the variation of R and σ with x will be the following. As the system is heated from very low temperatures R and σ will decrease smoothly until x reaches the value corresponding to the point E on the free energy curve. At this temperature R will suddenly decrease from some finite value to zero and σ will decrease to some value between .2 and zero. As the temperature is raised still further R will remain equal to zero and σ will gradually tend to zero. The temperature corresponding to the point E is thus the transition temperature.

Since m is dependent on σ and since σ is discontinuous at the transition temperature (at x_c) there will be a discontinuity in m, and hence in the volume of the system, at

$x = x_c$. There will also be a discontinuity in the energy of the system at $x = x_c$. Thus the inclusion of the volume change effect can alter the nature of the transition, giving a first order instead of a second order transition.

We have calculated the values of x_c for various pairs of values of Θ and ϕ, and these are set forth in Table I on page 46. It can be seen from this table that the larger values of Θ tend to reduce the effect of including the volume changes in the model. This is what one might expect as the larger the value of Θ for a given value of ϕ the larger is the quantity $V_o'-V_o$ and the smaller in proportion is the contribution of the variable part of the quantity $V_{AA}-V_{AB}$. When $V_o'-V_o$ is sufficiently large the system will behave as though the energy difference $V_{AA}-V_{AB}$ were essentially constant and, as mentioned earlier, a second order transition will result. We show in Figure 19a the variation of x_c with ϕ for constant Θ, and in Figure 19b the variation of x_c with Θ for constant ϕ. The variation is not far from linear, especially in the x_c versus Θ case.

We denote by R_- the value of the long range order just below the transition temperature and by σ_- and σ_+ the values of the short range order just below and just above the transition temperature. The values of R_- for the various pairs of values of Θ and ϕ are set down in Table II on page 47, and the values of σ_- and σ_+ are set down in

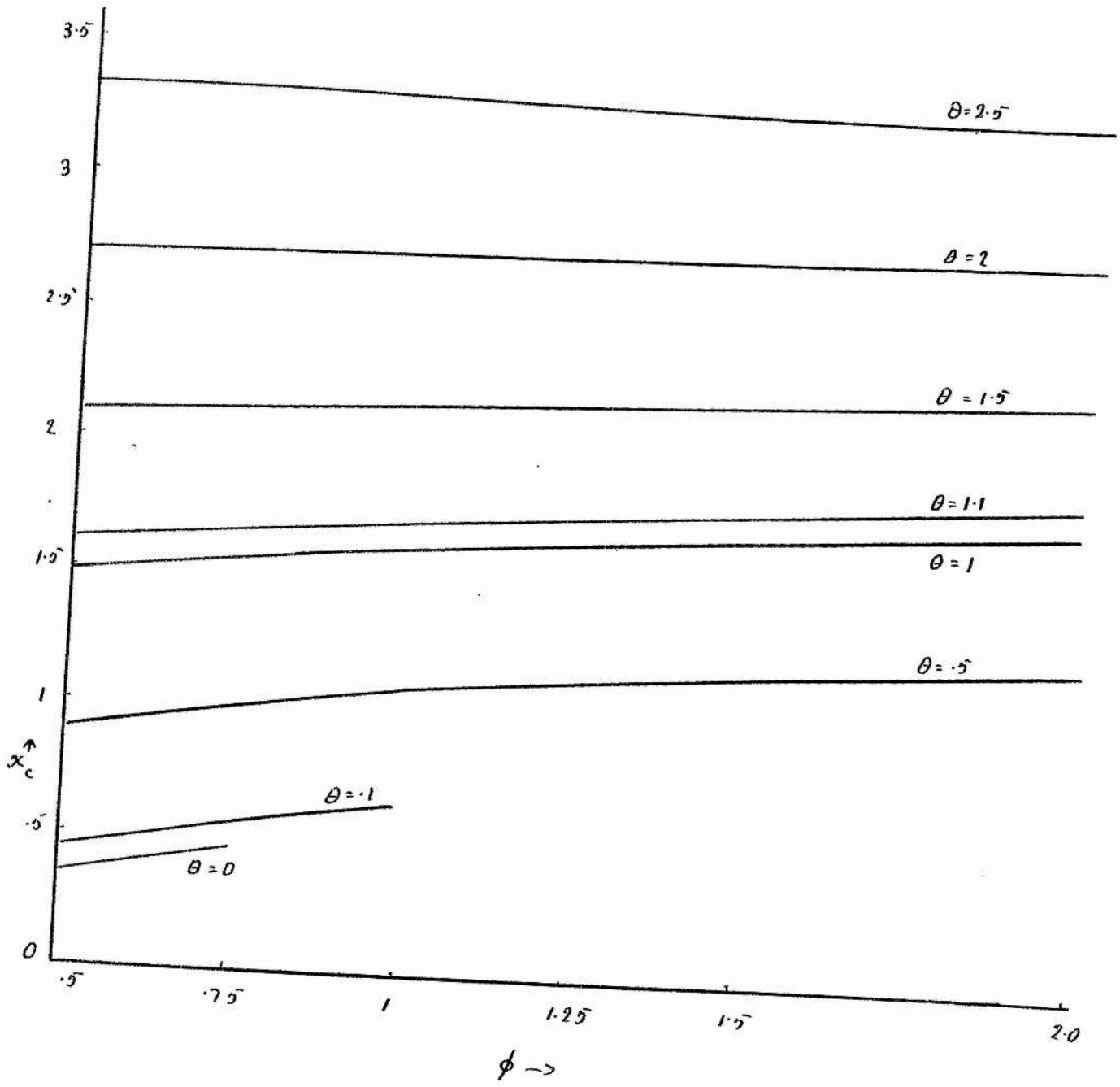


Figure 19a

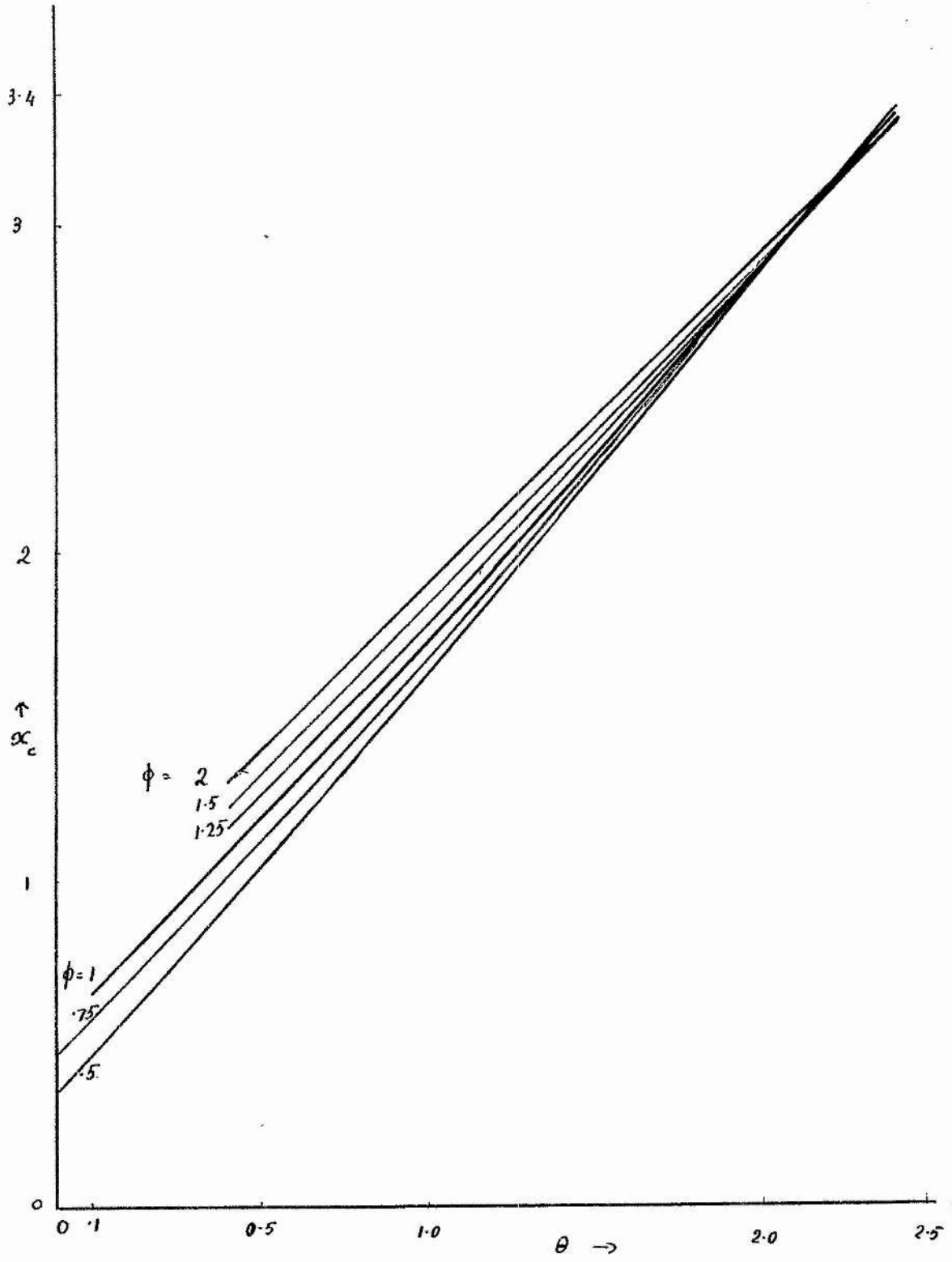


Figure 19b

TABLE I

x_c vs θ and ϕ for $z = 6$.

θ \ ϕ	0.50	0.75	1.00	1.25	1.50	2.00
0.0	.365	.469	For these values of θ and ϕ the condition $\theta > \phi(\phi-1)/(1+\phi)^2$ is not satisfied.			
0.1	.472	.575	.653			
0.5	.918	1.002	1.073	1.131	1.181	1.257
1.0	1.507	1.559	1.610	1.654	1.696	1.767
1.1	1.628	1.674	1.718	1.761	1.800	1.868
1.5	2.1195*	2.139	2.164	2.191	2.222	2.277
2.0	2.7360*	2.741	2.741	2.748	2.760	2.793
2.5	3.3526*	3.3569*	3.335	3.321	3.315	3.321

*(For these pairs of values of θ and ϕ the nature of the transition is unaltered.)

TABLE II

R_- vs θ and ϕ for $z = 6$.

θ \ ϕ	0.50	0.75	1.00	1.25	1.50	2.00
0.0	.936	.975				
0.1	.898	.959	.982			
0.5	.715	.874	.938	.967	.982	.992
1.0	.432	.736	.858	.920	.952	.981
1.1	.350	.707	.841	.908	.944	.977
1.5	.0	.565	.758	.858	.909	.961
2.0	.0	.300	.622	.765	.850	.933
2.5	.0	.0	.420	.650	.772	.887

TABLE III

$\frac{\sigma_-}{\sigma_+}$ vs θ and ϕ for $z = 6.$

θ \ ϕ	0.50	0.75	1.00	1.25	1.50	2.00
0.0	.885 .122	.953 .058				
0.1	.824 .156	.924 .106	.964 .062			
0.5	.581 .192	.786 .173	.887 .154	.938 .128	.965 .107	.984 .073
1.0	.335 .1994	.605 .193	.764 .181	.859 .169	.912 .156	.963 .133
1.1	.288 .1998	.572 .194	.740 .185	.839 .173	.898 .162	.957 .140
1.5	.2 .2	.434 .198	.632 .193	.764 .186	.841 .178	.927 .162
2.0	.2 .2	.264 .1995	.485 .198	.640 .194	.752 .189	.879 .178
2.5	.2 .2	.2 .2	.327 .1996	.512 .198	.649 .195	.807 .188

Table III on page 48. From these tables we see that, for given values of ϕ, an increase in θ gives lower values of R_- and of σ_- and higher values of σ_+. Thus the magnitude of the change of order of the system at the transition temperature is smaller the larger is the quantity θ. Tables II and III provide quantitative evidence of the general tendency towards a second order transition with increasing θ which was noted in connection with Table I.

The variation of R_-, σ_- and σ_+ with ϕ can be understood as follows. Consider the two systems defined by the inter-particle potential energies

1) $V_{AB} = V_o + D(r-r_o)^2$, $V_{AA} = V_{BB} = V_o' + D_1'(r-r_1)^2$;

2) $V_{AB} = V_o + D(r-r_o)^2$, $V_{AA} = V_{BB} = V_o' + D_2'(r-r_1)^2$;

where $D_1' > D_2'$, and hence $\phi_1 > \phi_2$. The energies of the two systems can be written in the form (using equation 3.6)

$$E_j = (Nz/4)(V_o'+V_o) + (Nz/4)D(r_1-r_o)^2[-\theta\sigma + \{\phi_j(1-\sigma)(1+\sigma)\}/\{1+\sigma+\phi_j(1-\sigma)\}].$$

When both systems are in the same state of order (i.e. characterised by the same value of σ) the difference in energy is given by

$$E_1 - E_2 = \frac{(Nz/4)D(r_1-r_o)^2(1-\sigma)(1+\sigma)^2(\phi_1-\phi_2)}{\{1+\sigma+\phi_1(1-\sigma)\}\{1+\sigma+\phi_2(1-\sigma)\}}$$

It follows, therefore, that the system with the larger value of $\emptyset$ has the greater energy for any given state of order and, as this energy is supplied in the form of heat, it will be at the higher temperature. Conversely, at any given temperature the system with the larger value of $\emptyset$ will have the greater degree of order. It is seen from Figure 19a that the transition temperature changes only slightly with $\emptyset$ (especially for the larger values of $\emptyset$) so that the change of order at the transition point should be greatest for the greatest values of $\emptyset$, as is found to be the case.

We wished also to calculate the expansion coefficient, $(\partial v/\partial T)/v$. We have

$$(\partial v/\partial T)/v = \{\partial(Nr^3)/\partial T\}/(Nr^3)$$

$$= [3(r_1-r_o)/\{r_o+m(r_1-r_o)\}](\partial m/\partial T).$$

Since we have neglected the effects of applied pressures we may replace $\partial m/\partial T$ by dm/dT. Also we may neglect the variation of the factor $\{r_o+m(r_1-r_o)\}$ compared with the variation of the factor dm/dT since (r_1-r_o) will be small compared to r_o (see page 1). Finally, since x is directly proportional to T, we have

$$(\partial v/\partial T)/v \propto dm/dx. \qquad 3.10$$

Equation 3.7 can be written as follows:

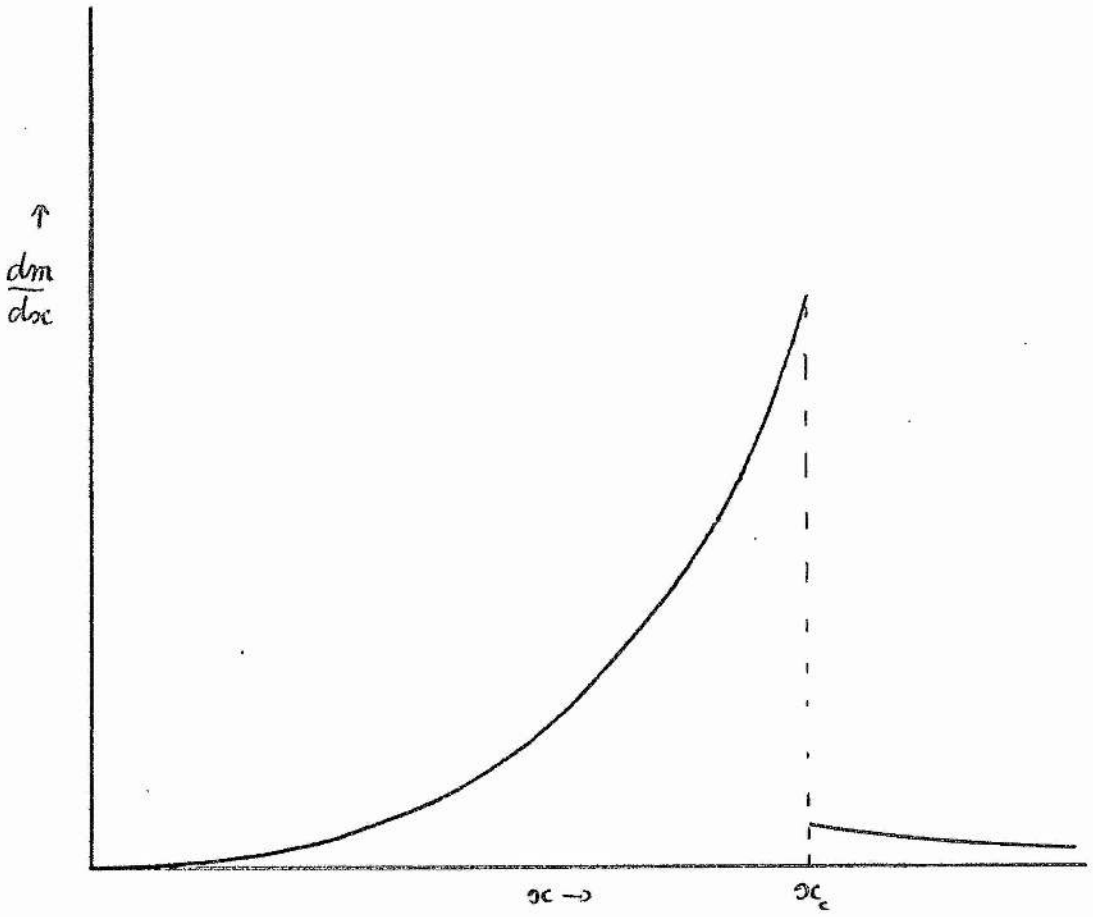


Figure 20

$$x = (\theta + \Phi)/M, \qquad \Phi = \phi\{(1+\sigma)^2 - \phi(1-\sigma)^2\}/\{1+\sigma+\phi(1-\sigma)\}^2,$$

whence we find

$$d\sigma/dx = M/\{(d\Phi/d\sigma) - x(dM/d\sigma)\}. \qquad 3.11$$

Also from equation 3.6 we have

$$dm/d\sigma = -2\phi/\{1+\sigma+\phi(1-\sigma)\}^2. \qquad 3.12$$

We calculated the quantities $d\sigma/dx$ and $dm/d\sigma$ given by equations 3.11 and 3.12 for the values of R and σ used in the previous calculations, and in this way obtained dm/dx ($= dm/d\sigma.d\sigma/dx$) as a function of x for each pair of values of the parameters θ and ϕ. We found generally that the variation of dm/dx with x was as shown in Figure 20. This anomalous expansion coefficient will, of course, be superimposed on the normal expansion coefficient of which we have taken no account in this chapter. In general the anomalous expansion will be very much smaller than the normal expansion for the greater part of the temperature range and for this reason we have not thought it necessary to give here our detailed results on the variation of dm/dx with x. We would, however, expect an observable effect in the region of the transition temperature below which dm/dx shows a rapid increase followed, as x passes x_c, by a sudden decrease to a much lower value. We have calculated the change in dm/dx across x_c for the various

values of Θ and $\emptyset$ and the results are set forth in Table IV on page 53. From this table we see that the change in the expansion coefficient at the transition temperature depends strongly on the energy difference $V_o'-V_o$ and on the relative slopes of the potential energy curves. In systems which show first order transitions the magnitude of the change is greatest when $V_o'-V_o$ is greatest and when the ratio D'/D is least. This follows since, when the transition is a first order one, the effect of increasing Θ is to give a smaller value of σ_- and the smaller value of σ_- corresponds to a steeper part of the curve of σ versus x (Figure 18a). Increasing $\emptyset$ has just the opposite effect.

For the pairs of values of Θ and $\emptyset$ which give a second order transition (i.e. $\emptyset = .5$, $\Theta = 1.5, 2.0, 2.5$ and $\emptyset = .75$, $\Theta = 2.5$) the behaviour is reversed. Here the main effect of increasing Θ is to increase the temperature scale and a given change in σ (and hence in m) takes place over a greater range of x. Also, since the system with the greater value of $\emptyset$ has a greater value of σ at any given temperature and since, in the case of systems with second order transitions, the transition temperature depends mainly on Θ and only very slightly on $\emptyset$, it follows that the slope of the σ versus x curve just above x_c (the value of σ at x_c being now always .2) must increase as $\emptyset$ increases, and hence the change in dm/dx increases as $\emptyset$

TABLE IV

$(dm/dx)_- - (dm/dx)_+$ vs θ and ϕ for $z = 6.$

θ \ ϕ	0.50	0.75	1.00	1.25	1.50	2.00
0.0	.345	.138				
0.1	.572	.202	.111			
0.5	1.67	.638	.299	.163	.094	.047
1.0	5.19	1.33	.665	.377	.237	.102
1.1	8.15	1.57	.750	.430	.270	.118
1.5	4.94	2.61	1.14	.653	.436	.202
2.0	1.38	9.74	2.16	1.09	.716	.338
2.5	.799	3.63	5.82	2.01	1.16	.539

increases.

We can obtain a rough estimate of the magnitude of the volume change effect as follows. Consider the case $\phi = 1$, $\theta = 1.5$, for which we have $x_c = 2.16$ and $\Delta(dm/dx) = 1.14$. The transition temperatures met with in practice are of the order of 700°A and hence, from the definition of x, we have

$$D(r_1-r_o)^2 = (kT_c/2x_c) \sim .014 \text{ ev},$$

and hence $V_o'-V_o \sim .021$ ev, which seems a reasonable value. Thus this combination of values of θ and ϕ might well be realised in the case of an alloy with a first order transition. We find in this case

$$(\partial v/\partial T)/v \sim 3(2.16/700)(1.14)(r_1-r_o)/r_o \sim 10^{-4} \text{ /degree},$$

since $(r_1-r_o)/r_o$ is of the order of one per cent. The coefficient of volume expansion of a typical metal, copper say, is about $.6(10^{-4})$ per degree at room temperature and increases only slightly with temperature. If we assume that the normal and anomalous effects are additive our model gives the result that the change in the expansion coefficient of a binary substitutional alloy AB at the transition temperature is comparable with the normal expansion coefficients of its constituent metals. Of course, the values set down in Table IV are obtained from the slopes of the m versus x curves taken at one point on the curves and will

be appreciably larger than any experimental value obtained by measuring the change in volume over a finite range of temperature. Also, because of the existence in an actual crystal of out-of-step domains of finite size which grow at the expense of one another during ordering or disordering, the transition is never infinitely sharp. The spreading of the transition over a small but finite range of temperature will also tend to reduce the change in the expansion coefficient. Notwithstanding these reductions, however, the volume change effect will still be considerable.

Another quantity of interest is the specific heat at constant pressure, C_p. We have

$$C_p = T(dS/dT) = x(dS/dx)$$

$$= x\{(\partial S/\partial R)(dR/dx) + (\partial S/\partial \sigma)(d\sigma/dx)\}.$$

The entropy, S, is given by the expression $S = k.\ln\{W(R,\sigma)\}$ and we use the quasi-chemical value of $W(R,\sigma)$ appearing on page 22. We note that the condition $\partial F/\partial R = 0$ reduces to $\partial S/\partial R = 0$ since E does not involve R. Finally, by using equation 3.7 to simplify the resultant expression for $\partial S/\partial \sigma$, we obtain C_p in a form suitable for calculation:

$$C_p = -(3Nk/4)(\theta + \Phi)(d\sigma/dx). \qquad 3.13$$

We found generally that the variation of C_p with x is

TABLE V

$(C_{p-} - C_{p+})/(Nk)$ vs θ and ϕ for z = 6.

θ \ ϕ	0.50	0.75	1.00	1.25	1.50	2.00
0.0	.67	.33				
0.1	1.03	.48	.28			
0.5	3.58	1.45	.72	.41	.25	.13
1.0	13.9	3.67	1.81	1.01	.62	.26
1.1	22.5	4.52	2.12	1.18	.72	.30
1.5	16.3	8.57	3.69	2.02	1.28	.54
2.0	5.88	36.5	8.07	3.90	2.43	1.61
2.5	4.17	16.0	24.7	8.28	4.53	1.85

quite similar to the variation of dm/dx with x shown in Figure 20, the dominant factor in both these quantities being dσ/dx. In Table V on page 56 we have set down the change in specific heat at the transition temperature. It is seen that $\Delta(C_p)/N$ is strongly dependent on the inter-particle forces in contrast with the normal quasi-chemical approximation which gives the unique value of (1.78)k per particle independent of the size of the quantity $V_o'-V_o$. The variations in Table V follow in the same way as those in Table IV.

3 The case z = 8.

In this case we find from equation 3.5 that as R tends to zero σ tends to the value 1/7. Using equation 3.7 we evaluated x as a function of R for the range $1 \geq R \geq 0$ and as a function of σ for the range R = 0, $1/7 \geq \sigma \geq 0$. We did not use such a large selection of variables θ and ∅ as in the case z = 6 since we expected the two cases to be very similar. In fact, for most pairs of values of θ and ∅, the variation of R and σ with x was again that shown in Figure 18a and the transition temperatures had to be found by comparing the free energies

$$F'(R) = \theta/4 + (\emptyset/2)(1+\sigma)^2/\{1+\sigma+\emptyset(1-\sigma)\}^2$$

$$- x[(1/4)\ln(2) + (7/8)\ln(1-R^2) - \ln(1-\sigma)], \quad 1 \geq R \geq 0,$$

and

TABLE VI

x_c vs θ and ϕ for z = 8.

θ \ ϕ	0.50	1.00	1.50
0.1	.638	.872	
0.5	1.257	1.449	1.583
1.0	2.078	2.192	2.294
1.5	2.937	2.966	3.021
2.0	3.806	3.773	3.773

TABLE VII

R_-, σ_- vs θ and ϕ for z = 8.
σ_+

θ \ ϕ	0.50	1.00	1.50
0.1	.904, .827 .106	.982, .966 .040	
0.5	.731, .580 .136	.939, .888 .104	.982, .965 .074
1.0	.473, .322 .142	.863, .763 .128	.952, .910 .110
1.5	.0 .1429 .1429	.762, .618 .137	.909, .835 .126
2.0	.0 .1429 .1429	.622, .455 .141	.848, .739 .134

TABLE VIII

$(dm/dx)_- - (dm/dx)_+$ vs θ and ϕ for z = 8.

θ \ ϕ	0.50	1.00	1.50
0.1	.425	.094	
0.5	1.07	.233	.083
1.0	2.79	.467	.184
1.5	7.80	.790	.322
2.0	1.20	1.55	.531

TABLE IX

$(C_{p-} - C_{p+})/(Nk)$ vs θ and ϕ for z = 8.

θ \ ϕ	0.50	1.00	1.50
0.1	.984	.259	
0.5	3.06	.714	.268
1.0	9.83	1.69	.625
1.5	32.5	3.37	1.25
2.0	6.51	7.63	2.39

$$F'(\sigma) = \Theta/4 + (\emptyset/2)(1+\sigma)^2/\{1+\sigma+\emptyset(1-\sigma)\}^2$$

$$- x[(1/4)\ln(2) - \ln(1-\sigma)], \qquad 1/7 \geqslant \sigma \geqslant 0.$$

The variation of x_c with Θ and $\emptyset$ is shown in Table VI on page 58. A comparison with Table I shows that for any given pair of values of Θ and $\emptyset$ the transition temperature is higher in the body-centred than in the simple cubic case. Indeed this must be so since the tendency towards order is enhanced by increasing the number of nearest neighbours per atom and hence more energy must be supplied to destroy the order.

In Table VII we have set down the values of R_-, σ_- and σ_+ for the various values of Θ and $\emptyset$. In most cases the values of R_- are almost equal to the corresponding values appearing in Table II. Thus when the transition is of the first order, the value of the long range order just below the transition temperature depends only slightly on whether the lattice is simple cubic or body-centred cubic. σ_- depends directly on z through equation 3.5 but the dependence turns out to be slight (c.f. Table III).

We used equations 3.11 and 3.12, with the values of M and x appropriate to the case z = 8, to calculate $d\sigma/dx$ and hence dm/dx and C_p. In this case we have, instead of equation 3.13, the following equation for C_p:

$$C_p = - Nk(\Theta + \dot{\Phi})(d\sigma/dx). \qquad 3.14$$

The results were very similar to those obtained for the simple cubic lattice and the discussion of the results in the previous section applies here also. In Tables VIII and IX we have set down the change in dm/dx and in C_p at the transition temperature for each pair of values of θ and ϕ. By comparing these tables with Tables IV and V respectively we can state the following general rule: If the inter-particle potential energy function is given then the change in the expansion coefficient (and in the specific heat) at the transition temperature is smaller for the body-centred cubic lattice than for the simple cubic lattice.

This rule can be understood as follows. Since the value of x_c for given θ and ϕ is greater for the case $z = 8$ than for the case $z = 6$ and since σ_- is not significantly changed then the magnitude of $d\sigma/dx$ ($x < x_c$) is smaller for $z = 8$ than for $z = 6$ and therefore both dm/dx and C_p will be smaller for the larger value of z. The change in dm/dx at x_c is almost equal to $(dm/dx)_-$ since $(dm/dx)_+$ is very much smaller than $(dm/dx)_-$ (and similarly for ΔC_p) so that the general rule follows.

The only tabulated exception to this rule occurs in the column $\phi = .5$ for the value $\theta = 1.5$, and this exception can be explained as follows. For both $z = 6$ and $z = 8$ the transition is a first order one when θ is small; the

magnitude of the change in R and in σ which occurs at the transition temperature decreases as Θ increases and eventually the transition becomes a second order one. The value of Θ (Θ say) for which this change in the nature of the transition occurs lies between 1 and 1.5 when Ø has the value .5. We have already noted (page 52) that $(dm/dx)_-$ increases as Θ increases to Θ' and decreases thereafter. In the case z = 6 the value of Θ' is sufficiently below 1.5 for a considerable decrease in $(dm/dx)_-$ to have taken place by the time Θ has increased from Θ' to 1.5. In the case z = 8, however, since Θ' is somewhat nearer the value 1.5, the resultant decrease in $(dm/dx)_-$ will be smaller. In fact the difference in the values of Θ'(z=6) and Θ'(z=8) is sufficient to ensure that, when Θ = 1.5, $(dm/dx)_-$ is greater for z = 8 than for z = 6. There will, of course, be a range of values of Θ about the value 1.5 for which this condition will hold. Similarly there are values of Θ which satisfy this condition for the other values of Ø. In all cases, however, the range of values of Θ for which the rule quoted on the previous page is not obeyed is only a small fraction of the total possible range of Θ.

We see from Table IX that the change in specific heat at the transition temperature depends strongly on the parameters describing the inter-particle forces. This is in contrast to the result obtained by applying the quasi-

chemical approximation to a body-centred cubic alloy of composition AB with constant inter-particle potential energies. In that case the change in specific heat at the transition temperature is 1.702.k per particle independent of the magnitude of the quantity $V_o'-V_o$.

4 Comparison with experiment.

We shall now apply our results to the case of an alloy which has been extensively studied, namely to the case of β-brass. Strictly speaking the phase range of β-brass extends only over the range of composition from 45.8 to 48.9 atomic per cent of zinc. As is usual, however, in the theoretical discussion of this alloy from the point of view of the order-disorder effect we shall neglect this small deviation from the ideal composition and consider β-brass to consist of equal numbers of copper and zinc atoms arranged on a body-centred cubic lattice.

We do not have sufficient information to enable us to write down explicitly the quantities V_{CuCu}, V_{ZnZn} and V_{CuZn}. We could obtain values of the atomic radii from X-ray data (though even here there is a difficulty in that the zinc lattice, which is classified as hexagonal close-packed, possesses an exceptionally large axial ratio and thus does not correspond to the hexagonal close-packing of spheres) but there is no direct way of finding well-defined values for the other parameters. As far as our

calculations are concerned, however, we require to know only those parameters which describe the Cu-Zn potential energy function relative to the average of the Cu-Cu and Zn-Zn potential energy functions, that is, Θ, ϕ and r_1-r_o. What we have done therefore is to use the experimental data on β-brass to obtain reasonable values of these three quantities and, with these values, to show that there results a consistent agreement with experiment.

The relevant experimental data are listed underneath:

1) β-brass exhibits a second order transition; the long range order decreases smoothly as the temperature is raised, reaches the value zero at $T_c = 742^oA$, and remains at this value above T_c.

2) There is an anomalous specific heat which rises sharply as T approaches T_c and suffers a discontinuous decrease as T passes T_c. The drop in specific heat at T_c has been found by Sykes and Jones [5] to be about 5.k per particle.

3) It has been shown (e.g. Steinwehr and Schulze, Phys. Zeits., 35, 1934, 385) that there is no discontinuity in the volume at T_c but that the expansion coefficient shows a sharp peak at T_c followed by a discontinuous drop as T passes through T_c.

The first of these facts gives us an indication as to the values which we must assign to Θ and ϕ. We see that most of the values appearing in Tables VI...IX could not

apply to the case of β-brass since the small values of Θ there give first order transitions. The actual values of Θ and Ø used here are Θ = 4.6 and Ø = 1. We chose Ø = 1 as we expect the slopes of the two potential energy curves, V_{CuZn} and $(V_{CuCu}+V_{ZnZn})/2$, near their minima to be very similar. The value of 4.6 for Θ was chosen to give agreement with the experimental value of 5.k per particle for the change in specific heat at the transition temperature.

Having thus assigned values to Θ and Ø we carried out the calculations as described in the previous sections. In Table X on page 66 we have set down the values of σ, m and x as functions of R below the transition temperature and the values of m and x as functions of σ above the transition temperature. In this case we find for x_c the value 8.243. Since $T_c = 742^oA$ we have $T_c/x_c = 90.0^o$ and hence

$$V_o' - V_o = \Theta D(r_1-r_o)^2 = \Theta kT_c/(2x_c) = .018 \text{ ev},$$

which seems to be a reasonable value.

The change in configurational energy in going from a state of complete order to a state of complete disorder is given by the expression

$$E/N = [E(\sigma=0) - E(\sigma=1)]/N = 2D(r_1-r_o)^2\{\Theta + (\Ø+1)/4\}$$

$$= .040 \text{ ev when } \Ø = 1 \text{ and } \Theta = 4.6.$$

This agrees well with the experimental value of .043 ev

TABLE X

R	σ	m	x
1.0	1.0	0.0	0.0
.99	.9804	.0098	4.130
.98	.9613	.0194	4.661
.97	.9426	.0287	5.020
.96	.9242	.0379	5.298
.95	.9063	.0469	5.526
.94	.8886	.0557	5.721
.93	.8712	.0644	5.890
.92	.8542	.0729	6.041
.91	.8374	.0813	6.176
.90	.8209	.0895	6.298
.85	.7424	.1288	6.775
.80	.6699	.1650	7.110
.75	.6030	.1985	71359
.70	.5413	.2293	7.550
.65	.4846	.2577	7.699
.60	.4327	.2837	7.818
.55	.3854	.3073	7.913
.50	.3426	.3287	7.989
.45	.3041	.3480	8.050
.40	.2699	.3651	8.099
.35	.2399	.3801	8.138
.30	.2140	.3930	8.170
.25	.1922	.4039	8.194
.20	.1744	.4128	8.213
.15	.1606	.4197	8.226
.10	.1507	.4246	8.236
.05	.1448	.4276	8.241
.00	.1429	.4286	8.243
	.14	.43	8.410
	.13	.435	9.042
	.12	.44	9.761
	.11	.445	10.66
	.10	.45	11.71
	.08	.46	14.59
	.06	.47	19.39

obtained by integrating the anomalous specific heat curve (c.f. Seitz, Modern Theory of Solids, page 379).

The coefficient of linear expansion, β, is given by

$$\beta = (1/r)(dr/dT) = (x_c/T_c)\{(r_1-r_o)/r_o\}(dm/dx).$$

We may compare our results with the experimental work of Steinwehr and Schulze who measured the linear expansion coefficient of a rod of β-brass over the temperature range from 20°C to 600°C. Their results were obtained by noting the change in length of the specimen over a considerable temperature interval, and the size of the interval varied between 100°C and 25°C. We have set down in column A of Table XI the experimental value of the linear expansion coefficient as a function of the temperature at the centre of each interval. The normal linear expansion coefficient of β-brass is $19(10^{-6})$ per degree at room temperature and rises nearly linearly to about $24(10^{-6})$ per degree at 900°A. In column B of Table XI we have set down the difference between the total expansion coefficient, which is what column A represents, and the normal expansion coefficient. The numbers in column C are the calculated values of dm/dx appropriate to the temperature T $(=xT_c/x_c)$ and column D contains the ratios of the values in column C to those in column B. If it is a good approximation to regard the normal thermal expansion and the anomalous

TABLE XI

	A	B	C	D
Temp. in °A.	Total β.	Anomalous β.	dm/dx.	Ratio C/B.
333	20.16(10^{-6})	.9(10^{-6})	.005	.006(10^{6})
423	22.37	2.3	.023	.010
523	24.04	3.1	.050	.016
623	28.67	7.0	.105	.015
686	30.88	8.6	.186	.022
701	39.52	17.2	.261	.015

(configurational) expansion as additive then, for our results to be in agreement with the experimental data, the numbers in column D should be approximately constant. In fact some of the experimental points lie a considerable distance from the smooth curve by which Steinwehr and Schulze represent their results so that the deviations from constancy in column D are not outwith the limits of the experimental error. The small values at the top of the column arise from the uncertainty as to the exact values of the normal expansion coefficient to be used in finding column B. Any error in this subtraction has its greatest effect at the lower temperatures. We have therefore taken $.015(10^6)$ as being the most probable value of the constant and have used this value to obtain the anomalous expansion coefficient from the calculated values of dm/dx. From equation 3.14 we find

$$(x_c/T_c)(r_1-r_o)/r_o = 1/\{.015(10^6)\},$$

and hence

$$(r_1-r_o)/r_o = 0.6\%.$$

This is the order of magnitude to be expected for the deviation from the rule of additivity of atomic radii in a substitutional alloy.

Table XII shows the theoretical anomalous expansion

coefficient as a function of the temperature and the results, and those of Steinwehr and Schulze, are shown graphically in Figure 21. Below the transition temperature the agreement between theory and experiment is good. Above T_c, however, the theoretical values are initially much smaller than the experimental results and it is not until a temperature considerably greater than T_c is reached that there is reasonable agreement between the two. This discrepancy (which cannot be removed merely by giving different values to the parameters θ, ϕ and r_1-r_o) may be due to the fact that any actual crystal consists of small grains. While each grain will have the value of R and of σ appropriate to the temperature the state at the grain boundaries will be rather complicated and for T greater than T_c there can still be regions with values of R greater than zero. The greater mobility of the atoms at the higher temperatures will tend to reduce the size of such regions thus giving a value to the expansion coefficient which is higher than the one calculated here on the assumption that a uniform state of order exists in all parts of the specimen.

We have also calculated the anomalous specific heat using equation 3.13 and the results are shown as a function of temperature in the last column of Table XII. Again we obtain good agreement with experiment at temperatures

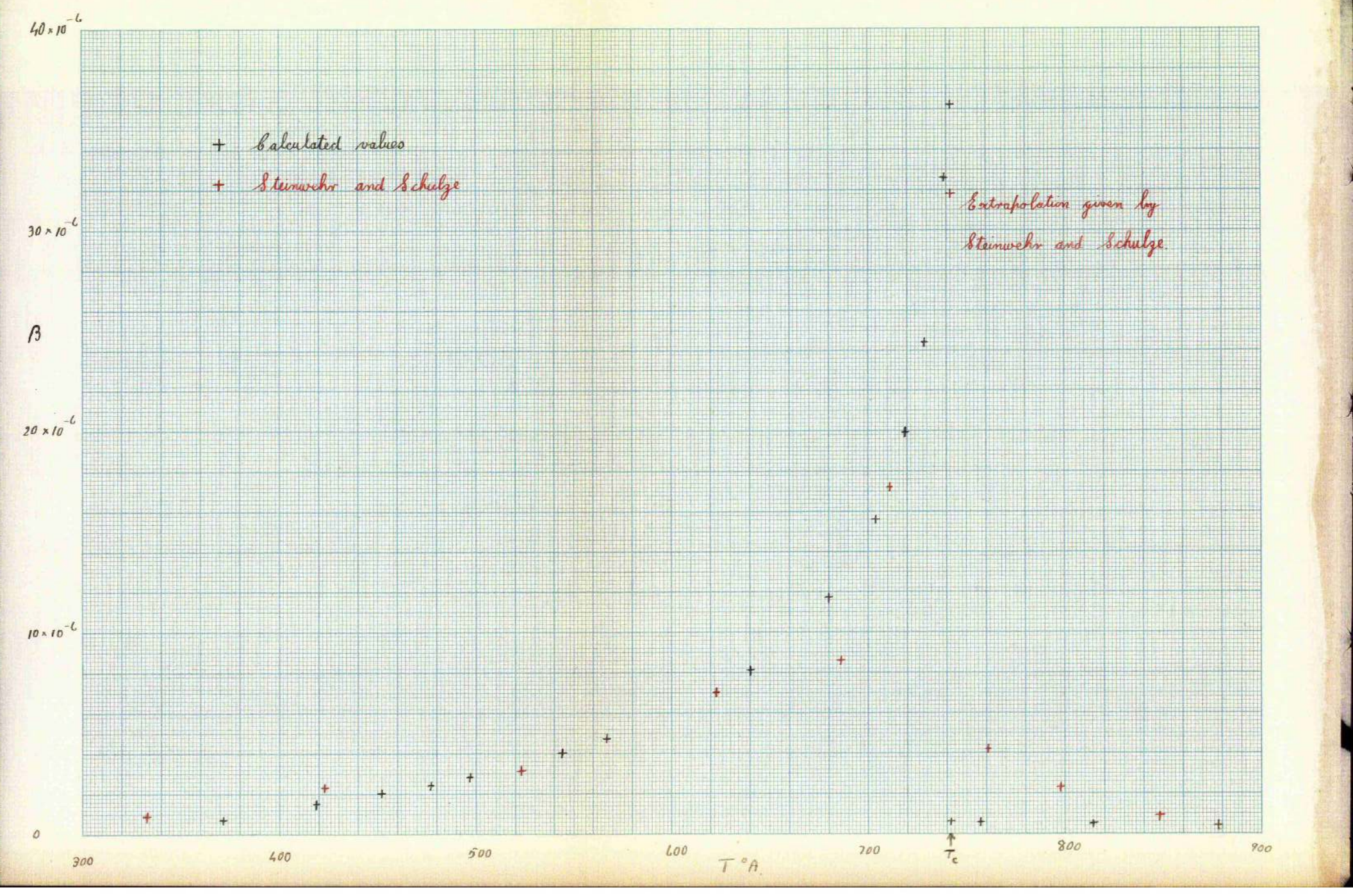

40 × 10⁻⁶
30 × 10⁻⁶
20 × 10⁻⁶
10 × 10⁻⁶
0
B
+ Calculated values
+ Steinwehr and Schulze
+ Extrapolation given by Steinwehr and Schulze.
300
400
500
600
700
800
900
T °A.
T_c

Figure 21.

TABLE XII

T	β	C_p/N
372°A	.7 per degree.	.16.k
419	1.5	.25
452	2.0	.30
477	2.4	.40
497	2.8	.47
544	4.0	.65
567	4.7	.76
640	8.1	1.28
680	11.7	1.81
704	15.6	2.36
719	19.9	2.95
729	24.4	3.56
739	32.6	4.67
742_-	36.2	5.15
742_+	.59	.084
757	.57	.081
814	.49	.069
878	.42	.059
960	.35	.049
1054	.29	.041

below the transition temperature but the calculated values above the transition temperature are too small. The considerations of the previous paragraph apply here also.

In Chapter V we derive an expression for the energy of vibration of an atom at the centre of a cell and we can use that result to write the vibrational frequency of the individual atoms in the form

$$f = (1/2\pi)(2zD/3M)^{1/2}, \qquad (M = \text{mass of the atom}).$$

Knowing T_c, x_c and $(r_1-r_o)/r_o$ enables us to calculate D and we find for f the value $18(10^{12})$ c.p.s. This, though a little high, is certainly of the right order of magnitude. We can compare this result with the value of f_{max} which appears in the Debye theory of the specific heat of a solid. For copper f_{max} has the value $6.8(10^{12})$ c.p.s. and for zinc f_{max} has the value $5.3(10^{12})$ c.p.s. The value for brass is somewhere between these limits. We could improve the agreement by considering other values of θ and ϕ (the value of $(r_1-r_o)/r_o$ for β-brass is more likely to be .015 than .006, and the appropriate choice of θ and ϕ would give the larger figure while still giving agreement with the data on the specific heat and expansion coefficient) but we consider that the agreement obtained above is ample illustration of the usefulness of our model and we have not thought it necessary to give any further details here.

Appendix to Chapter III

Strictly speaking, when dealing with a system whose volume is changing, we should consider the Gibbs function, $G = E - TS + pv$, rather than just the free energy, $F = E - TS$. As stated on pages 40 and 41, however, the atmospheric pressure, p, is small enough to be neglected in comparison with the other terms involved and we may show this quantitatively as follows.

$$v \sim Nr^3 \doteq Nr_o^3 + 3Nr_o^2(r_1 - r_o)m.$$

$$\therefore E + pv = (Nz/4)D(r_1 - r_o)^2 f_1 + 3Nr_o^2(r_1 - r_o)pf_2 + \text{constant},$$

where f_1 and f_2 are functions of σ of the same order of magnitude. Using the results obtained for β-brass we find that the ratio of the coefficients of the f_i is

$$[3Nr_o^2(r_1 - r_o)p]/[(Nz/4)D(r_1 - r_o)^2] \sim 2.10^{-5}$$

when p is the atmospheric pressure. Thus the contribution of the variable part of the term pv is negligible compared with that of the variable part of the configurational energy and hence our use of F rather than G is justified.

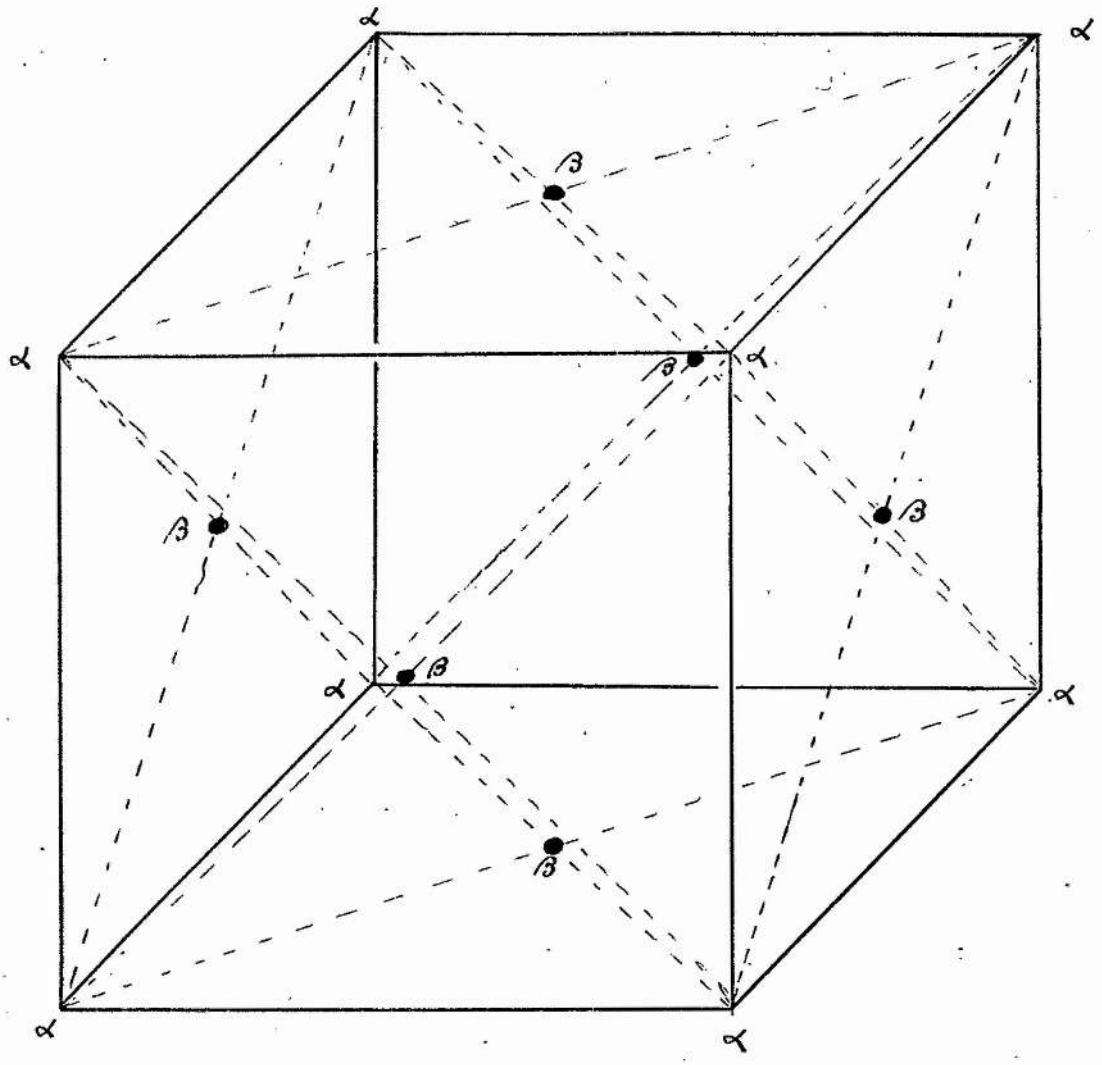


Figure 22.

IV

THE FACE-CENTRED CUBIC LATTICE.

1 We wish to consider here an alloy with the composition AB_3, the atoms being arranged to form a face-centred cubic lattice. The problem is complicated by the fact that each of the twelve nearest neighbours of a given site is a nearest neighbour of four of the others. We define the α-sites and β-sites as before, taking the arrangement at the absolute zero to be that in which the A atoms are on the cube corners and the B atoms are on the face-centres (see Figure 22), and in this case each α-site has twelve β-sites as its nearest neighbours, and each β-site has four α-sites and eight β-sites as its nearest neighbours.

In the simple cubic case and in the body-centred cubic case we found an expression of the form

$$\frac{Q_{\text{A on } \alpha,\ \text{B on } \beta} \cdot Q_{\text{B on } \alpha,\ \text{A on } \beta}}{Q_{\text{A on } \alpha,\ \text{A on } \beta} \cdot Q_{\text{B on } \alpha,\ \text{B on } \beta}} = \exp(J/kT).$$

Fowler and Guggenheim, in their book "Statistical Thermodynamics" state that the quasi-chemical method can be applied to the face-centred cubic lattice and leads to a pair of independent equations of this type. Although the calculations had not then been done, it was expected that straightforward, if tedious, numerical solution of these equations would give the equilibrium properties of the

assembly. Peierls, however, had stated in 1936 that the quasi-chemical method could not be applied to this case and later Li (1949) also arrived at this conclusion. As we were unable to find a detailed treatment which might indicate where the method broke down, we thought it worth while to carry out the calculations and to look for a possible modification which might give positive results.

The first approach was to consider the seven different types of nearest neighbour pair which can arise from the given definition of the α- and β- sites. The numbers of each type of pair are written as follows:

$Q_1 = Q_{A \text{ on } \alpha,\ A \text{ on } \beta}$ $\quad$ $Q_5 = Q_{A \text{ on } \beta,\ A \text{ on } \beta}$

$Q_2 = Q_{A \text{ on } \alpha,\ B \text{ on } \beta}$ $\quad$ $Q_6 = Q_{B \text{ on } \beta,\ B \text{ on } \beta}$

$Q_3 = Q_{B \text{ on } \alpha,\ A \text{ on } \beta}$ $\quad$ $Q_7 = Q_{A \text{ on } \beta,\ B \text{ on } \beta}$

$Q_4 = Q_{B \text{ on } \alpha,\ B \text{ on } \beta}$

Let there be N/4 A atoms and 3N/4 B atoms in the assembly. The long range order, R, is defined by putting the number of A atoms on α-sites equal to $N(1+3R)/16$. As usual R = 1 denotes complete order (all the A atoms on the α-sites), and R = 0 denotes disorder (probability of finding an A atom on an α-site equals the probability of finding an A atom on a β-site). In terms of R we have for the numbers of A and B atoms on the α- and β-sites the expressions

$$N_{A\alpha} = N(1+3R)/16, \qquad N_{A\beta} = 3N(1-R)/16,$$

$$N_{B\alpha} = 3N(1-R)/16, \qquad N_{B\beta} = 3N(3+R)/16.$$

There are four conditions which the Q_i must satisfy.

1) The total number of nearest neighbour pairs of which one of the sites is an α-site and the other is a β-site is easily seen to be 3N:

$$\therefore \quad Q_1 + Q_2 + Q_3 + Q_4 = 3N.$$

2) The total number of nearest neighbour pairs of which both sites are β-sites is also equal to 3N:

$$\therefore \quad Q_5 + Q_6 + Q_7 = 3N.$$

3) The total number of nearest neighbour pairs which have a B atom on an α-site is $z.N_{B\alpha}$ (z = 12 in this case):

$$\therefore \quad Q_3 + Q_4 = 9N(1-R)/4.$$

4) The total number of nearest neighbour pairs which have an A atom on a β-site is $z.N_{A\beta}$:

$$\therefore \quad Q_1 + Q_3 + 2Q_5 + Q_7 = 9N(1-R)/4.$$

The factor 2 in front of Q_5 in this last equation appears since to each (A on β, A on β) pair there are two A atoms on β-sites.

We collect these four equations in the form

$$Q_1 + Q_2 + Q_3 + Q_4 - 3N = 0 \qquad \ldots.A$$

$$Q_5 + Q_6 + Q_7 - 3N = 0 \qquad \ldots.B$$

$$Q_3 + Q_4 - 9N(1-R)/4 = 0 \qquad \ldots.C$$

$$Q_1 - Q_4 + 2Q_5 + Q_7 = 0 \qquad \ldots.D$$

We have to find the number of ways of obtaining a given distribution of the Q_i, and to do this we use the quasi-chemical approximation,

$$W(R,Q_i) = W'(R).(Q!)/\{\prod_i(Q_i!)\}, \qquad (i=1\ldots7)$$

where $Q = zN/2 = 6N$, and $W'(R)$ depends on R only. As before we replace $W'(R)$ by $W(R).\{\prod_i(Q_i'!)\}/(Q!)$, where the quantities Q_i' are the values of the Q_i which maximise $W(R,Q_i)$, and $W(R)$ stands for the expression

$$\frac{(N/4)!}{[N(1+3R)/16]!\,[3N(1-R)/16]!}\cdot\frac{(3N/4)}{[3N(3+R)/16]!\,[3N(1-R)/16]!}.$$

We have therefore to maximise $W(R,Q_i)$ with respect to the Q_i subject to the four conditions A, B, C and D. Using the method of undetermined multipliers and the Sterling approximation for $\ln(x!)$ gives us the equations

$$1 + \ln(Q_1') + A \qquad + D = 0$$

$$1 + \ln(Q_2') + A \qquad = 0$$

$$1 + \ln(Q_3') + A + C = 0$$

$$1 + \ln(Q_4') + A + C - D = 0$$

$$1 + \ln(Q_5') + B + 2D = 0$$

$$1 + \ln(Q_6') + B = 0$$

$$1 + \ln(Q_7') + B + D = 0$$

Eliminating A, B, C and D from these equations gives three independent equations which we can put in the form

$$Q_1'/Q_2' = Q_3'/Q_4' = Q_5'/Q_7' = Q_7'/Q_6'.$$

With these relations and the four equations A, B, C and D we can find the Q_i' as functions of R. We have to do this numerically, however, as follows. Let K represent the quantities Q_1'/Q_2' ..... The Q_i' can easily be expressed in terms of R and K using equations A, B and C, and then equation D gives us the relation between R and K. After simplification we find

$$R = \frac{3 - 2K - 10K^2 - 9K^3}{3 + 6K + 6K^2 + 3K^3},$$

and we used this relation to calculate R and Q_i' as functions of K.

The free energy of the system is given by

$$F = E(Q_i) - kT.\ln\{W(R,Q_i)\}$$

$$= V_{AA}(Q_1+Q_5) + V_{BB}(Q_4+Q_6) + V_{AB}(Q_2+Q_3+Q_7)$$

$$-kT[\ln\{W(R)\} + \sum_i Q_i'.\ln(Q_i') - \sum_i Q_i.\ln(Q_i)].$$

We considered first the case in which the quantities V_{AA}, V_{BB} and V_{AB} are constants. Hence the equilibrium states of the assembly are obtained by minimising F with respect to the eight variables R and Q_i subject to the four conditions A, B, C and D. We find

$$V_{AA} + kT[1 + \ln(Q_1)] + A + D = 0$$

$$V_{AB} + kT[1 + \ln(Q_2)] + A = 0$$

$$V_{AB} + kT[1 + \ln(Q_3)] + A + C = 0$$

$$V_{BB} + kT[1 + \ln(Q_4)] + A + C - D = 0$$

$$V_{AA} + kT[1 + \ln(Q_5)] + B + 2D = 0$$

$$V_{BB} + kT[1 + \ln(Q_6)] + B = 0$$

$$V_{AB} + kT[1 + \ln(Q_7)] + B + D = 0$$

$$-kT.\frac{d}{dR}[\ln\{W(R)\} + \sum_i Q_i'.\ln(Q_i')] + 9NC/4 = 0$$

Eliminating A, B, C and D from these equations gives

$$(Q_1.Q_4)/(Q_2.Q_3) = X, \quad (Q_5.Q_6)/(Q_7^2) = X, \qquad 4.1, 4.2$$

$$(Q_1/Q_2) = (Q_5/Q_7), \qquad 4.3$$

$$(Q_2/Q_3) = \exp\left\{\frac{4}{9N}\cdot\frac{d}{dR}\left[\ln\{W(R)\} + \sum_i Q_i'.\ln(Q_i')\right]\right\}. \qquad 4.4$$

X stands for the quantity $\exp(-J/kT)$. We mention in passing that equations 4.1 and 4.2 together form the pair of equations noted at the beginning of this chapter. Equation 4.4 simplifies to

$$(Q_2/Q_3) = [3(1-R)^2/(1+3R)(3+R)]^{1/12}.(Q_2'/Q') = P \text{ (say)}.$$

We used the tabulated values of R and the Q_i' to calculate the quantity P as a function of K. From equations A, B, C, D, 4.1, 4.2, 4.3, and 4.4 can be derived the equation

$$q_1^2(P-1) + q_1(\alpha P^2+3P-2\alpha P+3-\alpha) + P(9-P\alpha^2-\alpha^2) = 0,$$

where $q_1 = Q_1/N$ and $\alpha = 9(1-R)/4$, and this equation was used to calculate q_1 as a function of K, and hence as a function of R. It was found that, for values of R greater than .9573, q_1 was negative, increasing to zero at this value of R. In fact we require q_1 to be equal to zero when R = 1 and to increase as R decreases to zero. As we had expected that the values of the Q_i' which maximised $W(R;Q_i)$ would be the values corresponding to the random distribution of the A and B atoms appropriate to a given value of R we accordingly modified our attack.

2 Instead of considering the lattice as consisting of just two distinguishable types of site we now considered it as consisting of four distinguishable interpenetrating

lattices, the sites of which we denote by the symbols α, β, γ and δ. Thus each α-site has four β-, four γ- and four δ-sites as its nearest neighbours, and so on. We take the state at the absolute zero to be that in which the N/4 A atoms are all on the α-sites and the 3N/4 B atoms are shared equally among the β-, γ- and δ-sites. With this distinction among the lattice sites the number of types of nearest neighbour pair which we must consider is increased to twenty-four. We tabulate them as follows:

	$\alpha\beta$	$\alpha\gamma$	$\alpha\delta$	$\beta\gamma$	$\beta\delta$	$\gamma\delta$
AA	Q_1	Q_2	Q_3	Q_{13}	Q_{14}	Q_{15}
BB	Q_4	Q_5	Q_6	Q_{16}	Q_{17}	Q_{18}
AB	Q_7	Q_8	Q_9	Q_{19}	Q_{20}	Q_{21}
BA	Q_{10}	Q_{11}	Q_{12}	Q_{22}	Q_{23}	Q_{24}

Thus, for example, Q_1 is the number of nearest neighbour pairs which consist of an A atom on an α-site and an A atom on a β-site.

Because of the symmetry of the system with respect to the β-, γ- and δ-sites the following relations exist among the Q_i.

$$Q_1 = Q_2 = Q_3 = Na \qquad Q_4 = Q_5 = Q_6 = Nb$$

$$Q_7 = Q_8 = Q_9 = Nc \qquad Q_{10} = Q_{11} = Q_{12} = Nd$$

$$Q_{13} = Q_{14} = Q_{15} = Ne \qquad Q_{16} = Q_{17} = Q_{18} = Nf$$

$$Q_{19} = Q_{20} = Q_{21} = Q_{22} = Q_{23} = Q_{24} = Ng.$$

We use these relations to define the parameters a, b, c, d, e, f and g. Just as before there are four conditions which the Q_i must satisfy, and in terms of the parameters a, ..., g we find

$$a + c - (1+3R)/4 = 0 \qquad \ldots E$$

$$b + d - 3(1-R)/4 = 0 \qquad \ldots F$$

$$e + f + 2g - 1 = 0 \qquad \ldots G$$

$$a - b + e - f + 1 = 0 \qquad \ldots H$$

The number of ways of achieving a given distribution of the Q_i is again taken to be

$$W(R,Q_i) = W'(R).(Q!)/\{\prod_i(Q_i!)\}$$

$$= W(R).\{\prod_i(Q_i'!)\}/\{\prod_i(Q_i!)\},$$

or in terms of a, ..., g,

$$W(R,a..g) = W(R)\left\{\frac{(Na^{\times})!\,(Nb^{\times})!\,(Nc^{\times})!\,(Nd^{\times})!\,(Ne^{\times})!\,(Nf^{\times})!\,\{(Ng^{\times})!\}^2}{(Na)!\,(Nb)!\,(Nc)!\,(Nd)!\,(Ne)!\,(Nf)!\,\{(Ng)!\}^2}\right\}^3$$

W(R) is unchanged and $a^{\times}$, ..., $g^{\times}$ are the values of a, ..., g which maximise W(R,a..g) subject to the conditions E, F, G and H. This maximisation gives

$$a^{\times}/c^{\times} = d^{\times}/b^{\times} = e^{\times}/g^{\times} = g^{\times}/f^{\times} = K \text{ (say)}.$$

These equations are similar to those obtained in section 1 but now the relationship between K and R is simply

$$K = (1-R)/(3+R),$$

and the values of $\hat{a}$, ..., $\hat{g}$ are those which we had expected to find, namely

$\hat{a} = (1+3R)(1-R)/16$, $\hat{b} = 3(1-R)(3+R)/16$,

$\hat{c} = (1+3R)(3+R)/16$, $\hat{d} = 3(1-R)^2/16$,

$\hat{e} = (1-R)^2/16$, $\hat{f} = (3+R)^2/16$,

$\hat{g} = (1-R)(3+R)/16$.

After simplification $\ln\{W(R,a..g)\}$ becomes

$$11N[(1/4).\ln(3) - \ln(4)] +$$

$$33N[\{(1/3)+R\}\ln\{(1/3)+R\} + (3+R)\ln(3+R) + 2(1-R)\ln(1-R)]/16$$

$$- 3N[a.\ln(a) + ... + f.\ln(f) + 2g.\ln(g)].$$

The energy of the system is

$$E = 3N[(a+e)V_{AA} + (b+f)V_{BB} + (c+d+2g)V_{AB}]$$

$$= 3N[V_{BB} + V_{AB} + (a+e)J].$$

In the case where the interparticle potential energies are assumed constant we have to minimise the free energy with

respect to R, a, ..., g subject to the conditions E, F, G and H. The free energy is given by the expression

$$F(R,a..g) = E(a,e) - kT.\ln\{W(R,a..g)\}$$

and a straightforward calculation yields the equations

$$(a.b)/(c.d) = \exp(-J/kT), \quad a/c = e/g, \quad b/d = f/g,$$

$$d/c = [3(1-R)^2/(1+3R)(3+R)]^{11/12} = P \text{ (say)}.$$

These equations enable us to calculate a, ..., g as functions of R. Let β stand for $(1+3R)/4$. We find for c

$$c = [2\beta - (1-\beta-\beta P)/(1-\beta+\beta P)]/(1-P).$$

For values of R which are nearly equal to unity c turns out to be greater than β, and since $a+c = \beta$ it follows that a is negative. We note that a corresponds to the parameter q_1 of section 1. Thus, although the modification does give the values to a^x, ..., g^x corresponding to the random distribution of A and B atoms appropriate to a given value of R, the method still does not give a stable superlattice with R = 1 at the absolute zero.

3 Yang and Li (1945, 1947) applied the quasi-chemical method, not to pairs of neighbouring sites, but to tetrahedral quadruplets of sites and found that this procedure predicted a stable superlattice at low temperatures and an order-disorder transition. Each tetrahedral group has one

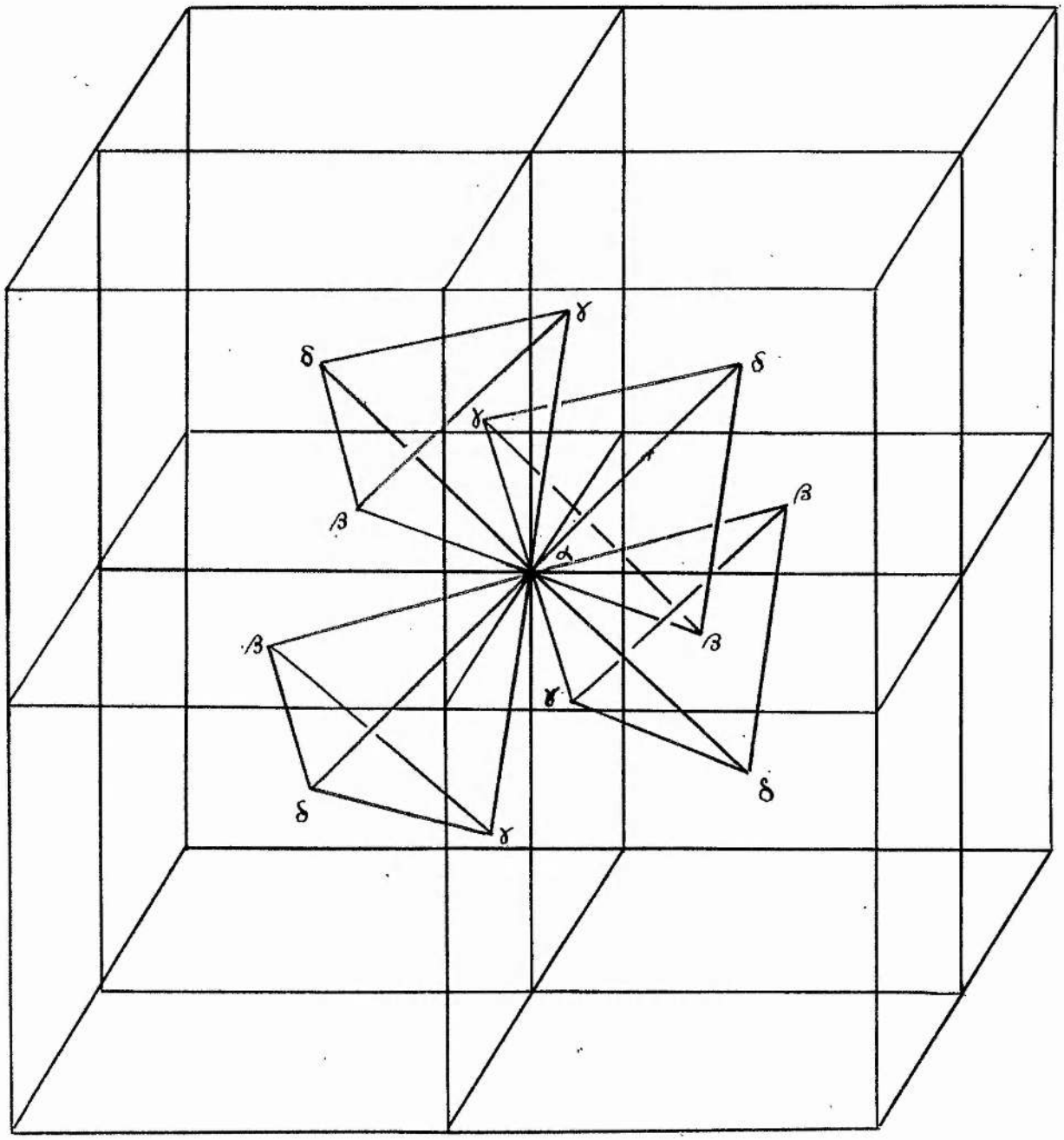


Figure 23.

site on each of the four sublattices α, β, γ, δ, and may be regarded as the characteristic group defining the superlattice. Li (1949) has given a criterion for determining whether one group of sites or another should give the better approximation when the quasi-chemical method is applied. A given group, G_1, will give a result that is not less accurate than that given by another group, G_2, if $zn_1/2p_1 < zn_2/2p_2$, where n is the number of sites in the group and p is the number of nearest neighbour pairs in the group. In sections 1 and 2 we had n = 2, p = 1, and thus zn/2p = 12. For the tetrahedral group n = 4, p = 6, and hence zn/2p = 4. This latter group should therefore give a much better approximation.

Another method of looking at this is the following. As soon as we fix the nature of the occupation of a certain pair of sites we limit the possible manners of occupation of those pairs which share a site with the first pair, and the closer those pairs are interlinked the worse will be the approximation. Also it is obvious that the more pairs which share a given site the worse will be the approximation. If we take the pair as the characteristic group then the number of groups which share a given site is 12, whereas if the tetrahedral group is taken this number is reduced to four. Figure 23 shows how the tetrahedral groups are situated with respect to one another.

If, as in section 1, we consider the lattice as having just two distinguishable types of site labelled α or β according to whether they are occupied by A or B atoms at the absolute zero, then each tetrahedral group would be composed of one α-site and three β-sites. In this case there are eight different ways of assigning four atoms to each group and we define eight parameters to describe the assembly as follows.

Manner of occupation.				Number of groups so occupied.
α	β	β	β	
A	B	B	B	Na
A	A	B	B	Nb
A	A	A	B	Nc
A	A	A	A	Nd
B	A	A	A	Ne
B	B	A	A	Nf
B	B	B	A	Ng
B	B	B	B	Nh

N is the total number of sites in the lattice. The number of tetrahedral groups which is necessary to include every nearest neighbour pair once and only once is easily seen to be equal to N. Hence we have

$$a+b+c+d+e+f+g+h = 1 \qquad \ldots I$$

The condition that there are $N(1+3R)/16$ A atoms on α-sites gives the equation

$$a+b+c+d = N(1+3R)/4. \qquad \ldots L$$

The condition that there are $N/4$ A atoms in the system gives the equation

$$a+2b+3c+4d+3e+2f+g = 1. \qquad \ldots M$$

Applying the quasi-chemical approximation for the number of ways of obtaining a given distribution of the groups gives us

$$W(R,a..h) = W(R).\frac{(N\check{a})!\,(N\check{b})!\,(N\check{c})!\,(N\check{d})!\,(N\check{e})!\,(N\check{f})!\,(N\check{g})!\,(N\check{h})!}{(Na)!\,(Nb)!\,(Nc)!\,(Nd)!\,(Ne)!\,(Nf)!\,(Ng)!\,(Nh)!}$$

$W(R)$ is as before and $\check{a}$, .., $\check{h}$ are the values of a, .., h which maximise $W(R,a..h)$ subject to the conditions I, L and M. It was found that these values were not the values corresponding to a random distribution of the A and B atoms appropriate to a given value of R, and accordingly we have again to consider the β-sites as lying on three distinguishable sublattices β, γ, δ. In this case there are sixteen distinguishable ways of assigning four atoms to each group but because of the symmetry of the system with respect to the β-, γ- and δ-sites the number of parameters needed to describe the occupation of the groups is reduced to eight. These correspond to the parameters

which appeared above.

The following table shows the different ways in which the tetrahedral groups may be occupied, the number of groups occupied in each way, and the total energy of each type of group.

Occupation. α β γ δ	Number so occupied.	Total energy of such groups.
A B B B	Na	$Na.3(V_{BB}+V_{AB})$
A A B B	Nb	$Nb.(V_{AA}+V_{BB}+4V_{AB})$
A B A B	Nb	"
A B B A	Nb	"
A A A B	Nc	$Nc.3(V_{AA}+V_{AB})$
A A B A	Nc	"
A B A A	Nc	"
A A A A	Nd	$Nd.6V_{AA}$
B A A A	Ne	$Ne.3(V_{AA}+V_{AB})$
B B A A	Nf	$Nf.(V_{AA}+V_{BB}+4V_{AB})$
B A B A	Nf	"
B A A B	Nf	"
B B B A	Ng	$Ng.3(V_{BB}+V_{AB})$
B B A B	Ng	"
B A B B	Ng	"
B B B B	Nh	$Nh.6V_{BB}$

The condition that there are N tetrahedral groups gives

$$a + 3b + 3c + d + e + 3f + 3g + h = 1 \qquad \ldots U$$

The condition that there are $N(1+3R)/16$ A atoms on α-sites gives

$$a + 3b + 3c + d - (1+3R)/4 = 0 \qquad \ldots V$$

Finally the condition that there are $N/4$ A atoms in the system gives

$$a + 6b + 9c + 4d + 3e + 6f + 3g = 1 \qquad \ldots W$$

Applying the quasi-chemical approximation for the number of ways of obtaining a given distribution of the sizteen distinguishable types of group gives us the following expression for $W(R,a..h)$

$$W(R).\frac{(Na^{\hat{}})!\{(Nb^{\hat{}})!\}^3\{(Nc^{\hat{}})!\}^3(Nd^{\hat{}})!(Ne^{\hat{}})!\{(Nf^{\hat{}})!\}^3\{(Ng^{\hat{}})!\}^3(Nh^{\hat{}})!}{(Na)!\{(Nb)!\}^3\{(Nc)!\}^3(Nd)!(Ne)!\{(Nf)!\}^3\{(Ng)!\}^3(Nh)!}$$

where $a^{\hat{}}$, ..., $h^{\hat{}}$, the values of a, ..., h which maximise $W(R,a..h)$ subject to the conditions U, V and W, are found to be

$$a^{\hat{}} = (1/2)^8(1+3R)(3+R)^3, \qquad b^{\hat{}} = (1/2)^8(1+3R)(3+R)^2(1-R),$$

$$c^{\hat{}} = (1/2)^8(1+3R)(3+R)(1-R)^2, \qquad d^{\hat{}} = (1/2)^8(1+3R)(1-R)^3,$$

$$e^{\hat{}} = (1/2)^8 3(1-R)^4, \qquad f^{\hat{}} = (1/2)^8 3(3+R)(1-R)^3,$$

$$g^{\hat{}} = (1/2)^8 3(3+R)^2(1-R)^2, \qquad h^{\hat{}} = (1/2)^8 3(3+R)^3(1-R).$$

After simplification we find for $\ln\{W(R,a..h)\}$ the expression

$$3N[(1/4)\ln(3) - \ln(4)] + (9N/16)[\{(1/3)+R\}\ln\{(1/3)+R\} + (3+R)\ln(3+R) + 2(1-R)\ln(1-R)] - N[a.\ln(a) + 3b.\ln(b) + 3c.\ln(c) + d.\ln(d) + e.\ln(e) + 3f.\ln(f) + 3g.\ln(g) + h.\ln(h)].$$

The configurational energy, E, is equal to

$$3N[(b+3c+2d+e+f)V_{AA} + (a+b+f+3g+2h)V_{BB} + (a+4b+3c+e+4f+3g)V_{AB}].$$

Using equations U, V and W enables us to write E in the more convenient form

$$E = 3N[V_{BB} + V_{AB} + (b+3c+2d+e+f)J],\ J = V_{AA} + V_{BB} - 2V_{AB}.$$

We now minimise the free energy, $F = E - kT.\ln\{W(R..h)\}$, with respect to the parameters R, a....h and r, where r is the lattice spacing, subject to the conditions U, V and W. The minimisation with respect to r gives simply $\partial E/\partial r = 0$ from which we find r as a function of the quantity $(b+3c+2d+e+f)$ once the dependence of V_{AA}, V_{BB} and V_{AB} on r is given. The minimisation with respect to the other parameters, using the method of undetermined multipliers,

gives the following set of equations:

$$(9/16)NkT.\ln[(1+3R)(3+R)/\{3(1-R)^2\}] - (3/4)V = 0$$

$$NkT\{1 + \ln(a)\} + U + V + W = 0$$

$$3NJ + 3NkT\{1 + \ln(b)\} + 3U + 3V + 6W = 0$$

$$9NJ + 3NkT\{1 + \ln(c)\} + 3U + 3V + 9W = 0$$

$$6NJ + NkT\{1 + \ln(d)\} + U + V + 4W = 0$$

$$3NJ + NkT\{1 + \ln(e)\} + U + 3W = 0$$

$$3NJ + 3NkT\{1 + \ln(f)\} + 3U + 6W = 0$$

$$3NkT\{1 + \ln(g)\} + 3U + 3W = 0$$

$$NkT\{1 + \ln(h)\} + U = 0.$$

Eliminating U, V and W from these equations gives

$$(c/b)^3 = d/a, \qquad (f/g)^3 = e/h, \qquad ac/b^2 = \exp(-J/kT),$$

$$g/a = e/c = f/b = [3(1-R)^2/\{(1+3R)(3+R)\}]^{3/4} \quad (= P \text{ say}).$$

These six equations together with the equations U, V and W determine the nine parameters R, a...h as functions of the temperature. For the purposes of calculation it is convenient to use R as the independent variable and to solve the equations in terms of the quantities s and t defined by the relations $b/a = s$ and $c/b = t$. The parameters b...h

are then given by

$b = sa$, $c = tsa$, $d = t^3a$, $e = Ptsa$, $f = Psa$, $g = Pa$,

$h = (Pt/s^2)a$.

Inserting thes values into equations U, V and W gives after simplification

$$a(3 + 3s + ts + t/s^2) = (1-\alpha)/P = A$$

$$a(1 + 3s + 3ts + t^3) = \alpha = B$$

$$a(1 + 2s + ts) = (4\alpha-1)/\{3(1-P)\} = C$$

where $\alpha = (1+3R)/4$. We find

$$s = (B - C - Ct^3)/\{3C - 2B + (3C - B)t\},$$

$$t = \{A - 3C + (2A - 3C)s\}s^2/\{C - (A - C)s^3\}.$$

The quantities A, B and C were evaluated as functions of R and the equations for s and t were then solved numerically. $\ln(ac/b^2)$ is equal to $\ln(t/s)$ so that we have

$$kT = J/\{\ln(s/t)\}. \qquad 4.5$$

We can use equations U, V, W and 4.5 to simplify the expression for the free energy and we find

$$F = 3N(V_{BB} + V_{AB}) - NkT[3\{(1/4)\ln(3) - \ln(4)\} - \ln(a) + (9/4)\{(1/3)\ln\{(1/3)+R\} + \ln(3+R)\}].$$

We have also to evaluate the free energy of the system when there is no long range order present. In this case the equations U, V and W can be written in the form

$$a + 3b + 3c + d = 1/4 \qquad U'$$

$$e + 3f + 3g + h = 3/4 \qquad V'$$

$$a + 6b + 9c + 4d + 3e + 6f + 3g = 1. \qquad W'$$

The expression for $\ln\{W(a...h)\}$ becomes

$$3N\{(3/4)\ln(3) - \ln(4)\} - N[a.\ln(a) + 3b.\ln(b) + 3c.\ln(c) + d.\ln(d) + e.\ln(e) + 3f.\ln(f) + 3g.\ln(g) + h.\ln(h)].$$

Minimising $F = E - kT.\ln\{W(a...h)\}$ gives eventually

$$(c/b)^3 = d/a, \qquad (f/g)^3 = e/h, \qquad ac/b^2 = \exp(-J/kT),$$

$$g/a = e/c = f/b, \qquad \partial E/\partial r = 0.$$

In this case it is convenient to use $X = \exp(-J/kT)$ as the independent variable for the calculation. We define the parameters u and v so that

$$b = ua, \; c = u^2Xa, \; d = u^3X^3a, \; e = vu^2Xa, \; f = vua, \; g = va,$$

$$h = (vX/u)a.$$

Equations U', V' and W' can now be written in the form

$$a(1 + 3u + 3u^2X + u^3X^3) = 1/4$$

$$a(u^2vX + 3uv + 3v + vX/u) = 3/4$$

$$a(3u + 6u^2X + 3u^3X^3 + 2vu^2X + 3vu - vX/u) = 0$$

from which we find

$$v = 1, \quad 3u^4X^3 + 8u^3X + 6u^2 - X = 0.$$

The latter result enables us to calculate u, and hence a...h, as a function of X. The result v = 1 gives a = g, c = e, b = f. It is obvious from the definitions of a...h that this should be so in the absence of long range order.

The free energy simplifies to

$$F = 3N(V_{BB} + V_{AB}) - NkT[3\{(3/4)\ln(3) - \ln(4)\} - \ln(a)],$$

and the transition temperature is found by comparing the two free energies.

In the approximation in which the dependence of the inter-particle potential energies on the lattice parameter is not taken into account we have simply

$$F'(R) = + kT[3.3348+\ln(a_R)-(9/4)\{(1/3)\ln\{(1/3)+R\}+\ln(3+R)\}]$$

$$F'(R=0) = + kT[1.6869 + \ln(a_{R=0})]$$

where $F' = [F - 3N(V_{BB} + V_{AB})]/N$. In this case the transition temperature is given by $kT/J = .4109$, and the value of the long range order just below the transition temperature is $R = .9557$.

We wish now to calculate the effect of including a volume dependent term in the free energy. As before we assume that the inter-particle potential energies can be written in the form

$$V_{AA} = V_A + D_A(r-r_A)^2, \qquad V_{BB} = V_B + D_B(r-r_B)^2,$$

$$V_{AB} = V_o + D(r-r_o)^2.$$

In the previous chapters, because of the symmetry of the systems considered, we could take $V_{AA} = V_{BB}$ with no loss in generality. This, however, is not the case here. The expressions which we have derived here for the free energy of the system in the two states R = R and R = 0 were based on the assumption that we were dealing with the alloy AB_3. To take $V_{AA} = V_{BB}$ would imply that exactly the same equations would hold also for the alloy A_3B and that therefore the transition temperatures of the two alloys would be equal. That this is not necessarily the case is exemplified by the copper-gold alloys. The transition temperature of the alloy $AuCu_3$ is 664°A while that of the alloy Au_3Cu is 516°A. To give a quite general treatment of the face-centred cubic alloy AB_3 it would be necessary to specify several parameters (instead of just two, θ and ϕ, as in the previous chapter) so that in what follows we shall restrict our attention to the copper-gold system.

The configurational energy of the alloy AB_3 has been

shown to be

$$E = 3N[V_{BB} + V_{AB} + (b+3c+2d+e+f)J].$$

The quantity $(b+3c+2d+e+f)$ approaches the value $1/8$ as the temperature increases to infinity so that the asymptotic value of E is

$$E = (3N/8)[V_{AA} + 9V_{BB} + 6V_{AB}]. \qquad 4.6$$

If the alloy is quenched from a temperature which is well above its transition temperature to a temperature well below then its configurational energy will be given by equation 4.6 to a high degree of approximation. The corresponding value of r (r_{AB_3} say) will be given by minimising equation 4.6 with respect to r. We find

$$D_A(r_{AB_3}-r_A) + 9D_B(r_{AB_3}-r_B) + 6D(r_{AB_3}-r_o) = 0. \qquad 4.7$$

Similarly we find for the alloy A_3B

$$9D_A(r_{A_3B}-r_A) + D_B(r_{A_3B}-r_B) + 6D(r_{A_3B}-r_o) = 0 \qquad 4.8$$

We may anticipate a little here and write down the asymptotic value of the configurational energy of the face-centred cubic alloy AB. We have

$$E = (3N/2)[V_{AA} + V_{BB} + 2V_{AB}]$$

so that in this case we have the relation

$$D_A(r_{AB}-r_A) + D_B(r_{AB}-r_B) + 2D(r_{AB}-r_o) = 0. \qquad 4.9$$

The lattice parameters of the pure metals and of the alloys are as follows:

Composition.	Lattice parameter, r.
Cu	3.608 Angstrom units.
Cu_3Au	3.750 " " . Quenched from 600°C
CuAu	3.867 " " " " "
$CuAu_3$	3.976 " " " " "
Au	4.070 " ".

(We have previously used r to denote the inter-particle spacing rather than the lattice parameter so that we should multiply these figures by the factor $2^{-1/2}$ before using them in our equations. We will assume, however, that this factor is absorbed in the D_i.) There is some slight uncertainty in these figures due to uncertainty as to the exact composition of the alloys for which they were measured but if we accept them we can insert them into equations 4.7, 4.8 and 4.9 and thus obtain values of D_A/D, D_B/D and r_o. To a good degree of approximation we find

$$D_{Cu}/D = .74, \qquad D_{Au}/D = 1.26, \qquad r_o = (r_A+r_B)/2 = 3.839,$$

and hence the inter-particle potential energies of the copper-gold alloys can be represented (in a manner which is consistent, in the nearest neighbour approximation,

with experimental data on the lattice parameters of the alloys) by the expressions

$$V_{AA} = V_A + D(.74)(r - 3.608)^2,$$

$$V_{BB} = V_B + D(1.26)(r - 4.070)^2, \qquad 4.10$$

$$V_{AB} = V_o + D(r - 3.839)^2.$$

The quantity J simplifies to

$$J = V' - D(.240)r, \qquad (V' = \text{constant}) \qquad 4.11$$

and the configurational energy becomes, in the case Cu_3Au,

$$E = 3N[V_1 + D(.74)(r - 3.608)^2 + D(r - 3.839)^2 + \gamma\{V' - D(.240)r\}], \quad \gamma = b+3c+2d+e+f, \quad V_1 = \text{const}$$

and in the case $CuAu_3$

$$E = 3N[V_2 + D(1.26)(r - 4.070)^2 + D(r - 3.839)^2 + \gamma\{V' - D(.240)r\}], \quad V_2 = \text{const.}$$

Hence, from the equation $\partial E/\partial r = 0$, we find

$$r = 3.741 + \gamma(.069), \qquad Cu_3Au \qquad 4.12$$

$$r = 3.968 + \gamma(.053), \qquad CuAu_3. \qquad 4.13$$

The quantity γ increases from zero when R = 1 to a maximum value of 1/8 at very high temperatures so that the total

change in volume when the alloy Cu_3Au goes from the disordered state to the ordered state is approximately .6% in good agreement with the results of Borelius et al.

We have therefore

$$J_1 = D[V'/D - .898 - .017\gamma] \qquad Cu_3Au \qquad 4.14$$

$$J_2 = D[V'/D - .952 - .013\gamma] \qquad CuAu_3 \qquad 4.15$$

and the free energies can now be written in the form

$$F_i'(R) = g_i(\gamma_R)^2 + [J_i/\ln(s/t)][3.3348 + \ldots.] \qquad 4.16$$

$$F_i'(R=0) = g_i(\gamma_{R=0})^2 + [J_i/\ln(s/t)][1.6869 + \ldots.] \qquad 4.17$$

where $g_1 = .0248$ and $g_2 = .0190$.

Following M. Shimoji (J. Phys. Soc. Japan 11, 91, 1956), who performed a similar calculation involving a simplifying assumption as to the dependence of the interchange energy on volume and thus obtained good agreement between the theoretical and experimental values of the ratio of the critical temperatures of the two alloys without, however, altering the details of the transition as described here on page 93, we may neglect the term in γ in the J_i and the term in γ^2 in the F_i' and we obtain the result

$$J_1/J_2 = T_{c1}/T_{c2}. \qquad 4.18$$

Experimentally we have $T_{c_1} = 664^\circ A$ and $T_{c_2} = 516^\circ A$ and we

can use these values with equation 4.18 to determine the value of the quantity V'/D. We find $V'/D = 1.143$ and hence

$$J_1 = D(.245 - .017\gamma), \qquad J_2 = D(.191 - .013\gamma). \qquad 4.19$$

As the largest value γ can have is .125 the terms in γ in the J_i are certainly negligible so that, after simplification, equations 4.16 and 4.17 become

$$F(R) = .1(\gamma_R)^2 + [1/\ln(s/t)][3.3348 + \ldots.] \qquad 4.20$$

$$F(R=0) = .1(\gamma_{R=0})^2 + [1/\ln(s/t)][1.6869 + \ldots.] \qquad 4.21$$

for both Cu_3Au and $CuAu_3$. The term in γ^2 does in fact make a very slight difference to the values of $[1/\ln(s/t)]$ and R_- at the transition point but essentially the theoretical description of the transition is as it was when the interparticle potential energies were taken to be independent of the atomic spacing. The extent of the agreement with experiment is confined to the (fitted) agreement with the ratio of the transition temperatures. In particular for the alloy Cu_3Au we found for R_- the value .9557 while the experimental value is given by Keating and Warren (J. Appl. Phys. 24, 52, 1953) as .80; the value of the anomalous linear expansion coefficient at T_c is about $2(10^{-6})$ while Nix (Phys. Rev. 60, 320, 1941) gives the values $\beta = 9.2(10^{-6})$ at 193°A, $\beta = 120(10^{-6})$ at T_{c-}, $\beta = 20(10^{-6})$ at T_{c+}. (Also the value of D_{Cu} turns out to be about .42 ev per

angstrom^2 as against the value 16.7 ev per angstrom^2 found from the results of the previous chapter. The difference is more than can be reasonably attributed to the approximations involved.) Thus the discrepancy between theory and experiment is such that either the abbove approach is invalid or the quasi-chemical method applied to tetrahedral groups of sites is not sufficiently accurate.

In order to discover whether a better agreement with experiment could be obtained within the framework of the quasi-chemical method we calculated R as a function of T using equation 4.5. We found that the variation of R with T was similar to that shown in Figure 18a; the point B on that figure corresponds here to a value of R in the region of .805. The free energy versus temperature curve is similar to that shown in Figure 18b; the point E on that curve corresponds here (when the dependence of the interparticle potential energies on the atomic spacing is neglected) to the value $R_- = .9557$. The presence of the term in γ^2 in equations 4.16 and 4.17 will alter the position of the point E. In fact the tendency is to make the point E approach the point B thus giving lower values of R_-, the magnitude of the change depending on the ratio g_i/J_i. In equations 4.20 and 4.21 this ratio had the value .1 and the change was negligible. If, however, we take g_i/J_i large enough we can make the point E approach the

point B as closely as we wish. Also as R decreases towards the value .805 the magnitude of the slope of the R versus T curve increases indefinitely and, since γ is a slowly varying function of R, $d\gamma/dT$ increases indefinitely. Thus it might be possible to find a value of β_- ($= (1/r)dr/dT_- = .0185 d\gamma/dT_-$) more in keeping with the value found by Nix.

We found that, if we gave the value .00543 to the quantity $V'/D = -.898$ which appears in J_1, the value of R_- became about .81 and the value of β_- became about $100(10^{-6})$ per degree. The calculations were approximate but suffice to show that it is possible, using our model, to obtain simultaneously values of R_- and β_- which are in reasonably good agreement with experimental data on the alloy Cu_3Au. In addition we now have D_{Cu} of the order of 18 ev per angstrom^2 agreeing quite well with the value 16.7 ev per angstrom^2 derived from the results of the previous chapter. In view of the numerical approximations made in the calculation, however, we do not attach any particular significance to this rather good agreement beyond noting that it makes this approach to the problem more plausible than the one discussed on pages 98 and 99.

We had hoped to use the value of $V'/D = -.898$ given above to obtain a value of J_2 from equation 4.15 and with this value to calculate the details of the order-disorder transition of the alloy $CuAu_3$. J_2 turns out to be negative,

however, and, as we must have a positive value for the interchange energy in order that there should be a transition from a fully ordered state to a disordered state as the temperature is raised, the attempt to describe the transitions of all three alloys, Cu_3Au, $CuAu_3$, CuAu, using just one set of values for the parameters which appear in equations 4.10 and 4.11 has to be abandoned. To describe the transition of the alloy $CuAu_3$ we would have to use a different value of the quantity V'/D (we would expect that here V'/D = .952 would be small and positive as was V'/D = .898 in the case Cu_3Au) but we have been unable to find sufficiently detailed experimental data on the alloy $CuAu_3$ and therefore we have not carried out any further calculations on this alloy.

As a final indication that the approach discussed on pages 98 and 99 is inadequate we give some results on the alloy CuAu. The calculations are similar to those for the other two alloys but are complicated by the fact that, since the ordered phase of CuAu is tetragonal, there are two nearest neighbour separations to be considered. We do not, however, propose to give the details here. Taking the value of V'/D which gives the correct result for the ratio of the transition temperatures of the alloys Cu_3Au and $CuAu_3$ (i.e. V'/D = 1.143) we found that the transition temperature of the alloy AuCu was equal to 611^{o}A, the

the value of R_- was .9744, and the axial ratio varied from 1.032 at low temperatures to 1.030 at the transition temperature. The experimental values are respectively T_c = 681°A, $R_- \doteq .97$, and the axial ratio varies from 1.080 at low temperatures to 1.075 at T_c. (Roberts, Acta Metal. 2, 597, 1954) We should at least have expected agreement between the theoretical and experimental values of the transition temperature but the agreement is generally rather poor.

Thus we arrive at the following conclusion. Ideally a theoretical description of the order-disorder transition in substitutional alloys should take into account the band structure of the alloys. For any given alloy, however, the essentials are quite well represented by two-body potential energy functions and it is only when we attempt to take the functions derived for one alloy as a representation of the band structure of another alloy (with the same components) that our model is liable to lead to incorrect results. It is therefore necessary to consider each alloy on its own merits and, with this restriction, we believe that, where sufficient experimental data on an alloy exist to enable us to give reasonably accurate values to the parameters needed in the definition of the two-body potential energy functions, our model gives results which are in good agreement with experiment.

V

THE EFFECT OF LATTICE VIBRATIONS.

1 As a solid is heated from very low temperatures the first effect is that the atoms are caused to vibrate about their mean positions in the lattice with an amplitude of vibration which increases with temperature. (We neglect the zero point vibrations.) Eventually enough energy will be concentrated on some atoms to cause them to move through the lattice and interchange positions and in this way the distribution of the atoms over the lattice sites is altered. In the previous chapters we have considered the equilibrium distributions of the A and B atoms over the lattice sites assuming that the atoms are at rest on the lattice sites. That is, we have assumed the equilibrium distributions to be quite independent of the atomic motions by which they may be realised. An obvious first refinement of the theory is to take into account the atomic vibrations and it is the purpose of this chapter to consider the effect of these vibrations on the order-disorder transition. We assume that the atoms are performing independent simple harmonic vibrations about their equilibrium positions. The neglect of any coupling between vibrations is equivalent to the Einstein treatment of specific heats which is quite adequate for the temperatures at which order-disorder transitions are likely to occur.

We consider here the case of a substitutional alloy of N/2 A atoms and N/2 B atoms distributed over the sites of a simple cubic or a body-centred cubic lattice. Using the notation given in the treatment of the quasi-chemical method in chapter I we have

$$N_{A\alpha} = N_{B\beta} = N(1+R)/4$$

$$N_{A\beta} = N_{B\alpha} = N(1-R)/4$$

$$Q_{AB} = Nz(1+2R+\sigma)/8, \quad Q_{BA} = Nz(1-2R+\sigma)/8 \qquad 5.1$$

$$Q_{AA} = Q_{BB} = Nz(1-\sigma)/8$$

where z is put equal to 6 or 8 depending on whether we are dealing with the simple cubic or body-centred cubic structures respectively.

On average each A atom on an α-site will have za A atoms and z(1-a) B atoms as its nearest neighbours. The fraction a is easily found as follows. Since the number of A atoms on α-sites is N(1+R)/4 the total number of A-A pairs is just za.N(1+R)/4. As the total number of A-A pairs is given also by Q_{AA} we must have

$$za.N(1+R)/4 = Nz(1-\sigma)/8$$

and hence $$a = (1-\sigma)/\{2(1+R)\}. \qquad 5.2$$

In exactly the same way we can find the fraction, b, which

is such that the average number of A atoms which are the nearest neighbours of an A atom on a β-site is zb. We find

$$b = (1-\sigma)/\{2(1-R)\}. \qquad 5.3$$

Because of the symmetry of the system with respect to the A and B atoms, za will also be the average number of B atoms among the nearest neighbours of a B atom on a β-site, and zb will be the average number of B atoms among the nearest neighbours of a B atom on an α-site.

Consider a group of atoms consisting of a central A atom on an α-site together with its z nearest neighbours. The potential energy of the central A atom when at rest on the α-site is

$$V_A^{\alpha}(r,0) = za.V_{AA}(r) + z(1-a).V_{AB}(r). \qquad 5.4$$

[We use the quantity $V_X^{\gamma}(r,p)$ to denote the average potential energy of an X (= A or B) atom when it is vibrating with amplitude of vibration p about its mean position on a γ-site (γ = α or β).] If we consider the potential energy given by 5.4 as arising from the presence of za A atoms each contributing an amount of energy $V_{AA}(r)$ and of z(1-a) B atoms each contributing an amount $V_{AB}(r)$, then the point at which the minimum value of $V_A^{\alpha}(r,0)$ occurs will not be at the centre of the group of sites but at some distance from it depending on the distribution of the

za A atoms and z(1-a) B atoms over the sites of the group and on the relative magnitudes of $V_{AA}(r)$ and $V_{AB}(r)$. This is inconsistent with our model of an assembly of atoms whose equilibrium positions are the α- and β-sites, the separation of the sites being uniquely determined at every temperature by the lattice parameter, r. We assume, therefore that the atomic wave functions, and hence the contribution of the individual atoms to the cohesive energy, are so modified in the solid state that we can consider each atom of the group of z atoms around a central A atom on an α-site as contributing an amount of energy

$$(1/z).V_A^{\alpha}(r,0) = a.V_{AA}(r) + (1-a).V_{AB}(r) \qquad 5.5$$

to the energy of the central A atom, and in this case the point of minimum potential energy does lie on the α-site.

We can now calculate the quantity $V_A^{\alpha}(r,p)$ as follows. Let the α-site be the origin of a set of axes parallel to the sides of the unit cube of the lattice, and consider the potential energy of the A atom when it is displaced to the point (x,y,z). For definiteness we treat here the case of the simple cubic lattice. As before we take

$$V_{AA} = V_{BB} = V_o' + D'(r-r_1)^2, \qquad V_{AB} = V_o + D(r-r_o)^2.$$

For the purpose of calculating the vibrational potential energy of the central atom the boundary atoms may be taken

to be at rest on their β-sites. We have then for $V_A^{\alpha}(r,xyz)$

$$a.V_{AA}(\{(r-x)^2+y^2+z^2\}^{1/2}) + (1-a).V_{AB}(\{(r-x)^2+y^2+z^2\}^{1/2})$$
$$+ a.V_{AA}(\{(r+x)^2+y^2+z^2\}^{1/2}) + (1-a).V_{AB}(\{(r+x)^2+y^2+z^2\}^{1/2})$$
$$+ a.V_{AA}(\{(r-y)^2+x^2+z^2\}^{1/2}) + (1-a).V_{AB}(\{(r-y)^2+x^2+z^2\}^{1/2})$$
$$+ a.V_{AA}(\{(r+y)^2+x^2+z^2\}^{1/2}) + (1-a).V_{AB}(\{(r+y)^2+x^2+z^2\}^{1/2})$$
$$+ a.V_{AA}(\{(r-z)^2+x^2+y^2\}^{1/2}) + (1-a).V_{AB}(\{(r-z)^2+x^2+y^2\}^{1/2})$$
$$+ a.V_{AA}(\{(r+z)^2+x^2+y^2\}^{1/2}) + (1-a).V_{AB}(\{(r+z)^2+x^2+y^2\}^{1/2}).$$

With the explicit form for V_{AA} we find that the first term, for instance, of the above expression becomes

$$a.[V_o' + D'\{r^2-2rx+x^2+y^2+z^2-2r_1(r^2-2rx+x^2+y^2+z^2)^{1/2}+r_1^2\}].$$

Let $x^2+y^2+z^2 = p^2$. Neglecting terms of order higher than the second order in the displacements x, y and z, we have

$$(r^2-2rx+p^2)^{1/2} = r\{1-(x/r)+([p^2-x^2]/[2r^2])\},$$

and the above term becomes

$$a[V_o' + D'(r-r_1)^2] + a.D'[-2x(r-r_1) + p^2 -(r_1/r)(p^2-x^2)].$$

The other terms involving V_{AA} are obtained from the first one by replacing x by -x, ±y, ±z, and similarly one can evaluate the terms involving V_{AB}. Collecting the terms gives finally

$$V_A^{\alpha}(r,p) = 6a.[V_o' + D'(r-r_1)^2 + D'\{1-(2r_1/3r)\}.p^2] +$$

$$6(1-a)[V_o + D(r-r_o)^2 + D\{1-(2r_o/3r)\}.p^2].$$

A similar result is found for the body-centred cubic case with 8 replacing the factor 6 above. The approximation made in neglecting terms of order higher than the second order in the displacements x, y, z in the expansion of $(r^2-2rx+p^2)^{1/2}$, etc., gives the same result as that given by assuming the z nearest neighbours of the central atom to be smeared out over the surface of a sphere of radius r, the contribution per unit area to the potential energy of the central atom being equal to

$$z[a.V_{AA} + (1-a).V_{AB}]/(4\pi r^2).$$

With this assumption $V_A^{\alpha}(r,p)$ is given by

$$(z/2)\int_0^{\pi} [a.V_{AA}(r') + (1-a).V_{AB}(r')].\sin\theta.d\theta,$$

where $r' = (r^2 - 2rp.\cos\theta + p^2)^{1/2}$. This is the expression used by Sarolea [42].

Thus we have $V_A^{\alpha}(r,p)$ as the sum of two terms

$$V_A^{\alpha}(r,0) + z[a.D'\{1-(2r_1/3r)\} + (1-a)D\{1-(2r_o/3r)\}].p^2.$$

Previously we had calculated the energy of the crystal in such a way that only the term $V_A^{\alpha}(r,0)$ was taken into account, and it is this term which gives rise to the

volume change effect described in chapter III. The other term is the contribution to the crystal energy arising from the atomic vibrations. Although this term will influence the volume change effect, since it contains r, yet the way in which r appears is such that the variation of volume with temperature already calculated is changed only by a small correction, and for simplicity we put $r_1/r = r_o/r = 1$ in this term. Hence

$$V_A^\alpha(r,p) = V_A^\alpha(r,0) + (z/3)[a.D' + (1-a).D].p^2. \qquad 5.6$$

As we have calculated it, the quantity $V_A^\alpha(r,p)$ is the potential energy of an A atom when it is displaced a distance p from its α-site. Such a variation of potential energy with displacement, however, gives rise to simple harmonic vibrations about the point $p = 0$, and if we take the average of the potential energy over the period of the vibration we find that it is given by equation 5.6 provided that we now define p to be the amplitude of the vibration.

In exactly the same way we can obtain expressions for the other quantities $V_X^\gamma(r,p)$. We find

$$V_A^\alpha(r,p) = V_B^\beta(r,p) = V_A^\alpha(r,0) + P_+.p^2,$$

$$V_A^\beta(r,p) = V_B^\alpha(r,p) = V_A^\beta(r,0) + P_-.p^2$$

where $V_A^\alpha(r,0)$ is given by equation 5.4 and $V_A^\beta(r,0)$ is a similar expression with b in place of a. P_+ and P_- are

given by

$$P_+ = (zD/3)[1 + a(\phi-1)], \quad P_- = (zD/3)[1 + b(\phi-1)], \quad 5.8$$

where $\phi = D'/D$. The quantities P_+ and P_- differ only in that $-R$ appears in P_- where $+R$ appears in P_+.

The vibrational partition function of an X atom on a γ-site will be denoted by Z_X^γ and is given by

$$Z_X^\gamma = \int_0^{r/2} 4\pi p^2 . \exp[-\{V_X^\gamma(r,p) - V_X^\gamma(r,0)\}/kT] . dp$$

$$= 4\pi \int_0^{r/2} \exp[-(P_\pm . p^2)/kT] . p^2 . dp. \qquad 5.9$$

We have taken the upper limit of the integral to be $r/2$ since it is reasonable to expect that the maximum possible amplitude of vibration in the solid state will be equal to half the interparticle spacing. If we now make the substitution $y^2 = P_\pm . p^2/kT$ equation 5.9 becomes

$$Z_X^\gamma = 4\pi(kT/P_\pm)^{3/2} . \int_0^L \exp(-y^2) . y^2 . dy,$$

where L stands for the quantity $(P_\pm r^2/4kT)^{1/2}$. As before we define x by the relation

$$x = kT/\{2D(r_1 - r_o)^2\}$$

and we find for L^2 the expression

$$L^2 = (z/24x) . [1 + (\phi-1)(1-\sigma)/\{2(1 \pm R)\}] . [r^2/(r_1 - r_o)^2] .$$

For very low temperatures $1/x$ will be large and we may replace the upper limit of the integral by infinity. For temperatures near the transition temperature we had, in the case of β-brass, $z = 8$, $x \sim 8$, $(r_1-r_o)/r_o = .006$, and $[1 + (\phi-1)(1-\sigma)/\{2(1\pm R)\}] \sim 1$. Thus at the transition temperature L is of the order of 30 and, since the value of the integral with its upper limit equal to 30 is practically equal to its value when the upper limit is infinite, we may replace the upper limit by infinity for all temperatures below the transition temperature and for at least part of the temperature range above it. This replacement of L by infinity, justified here for the values of the parameters used to describe the behaviour of β-brass, is in fact generally valid since the dominant factor in L is $r_o/(r_1-r_o)$ and we would not expect a value of $(r_1-r_o)/r_o$ greatly different from one per cent in the case of a substitutional alloy. Thus we have

$$Z_X^\gamma = (kT/P_\pm)^{3/2} . 4\pi . (\pi/16)^{1/2},$$

and hence

$$Z_A^\alpha = (\pi kT/P_+)^{3/2} = Z_B^\beta, \quad Z_A^\beta = (\pi kT/P_-)^{3/2} = Z_B^\alpha. \qquad 5.10$$

The vibrational partition function of the whole assembly is, therefore,

$$Z_{vib.} = (Z_A^\alpha)^{N_{A\alpha}} . (Z_B^\beta)^{N_{B\beta}} . (Z_A^\beta)^{N_{A\beta}} . (Z_B^\alpha)^{N_{B\alpha}}$$

$$= (Z_A^{\alpha}.Z_B^{\beta})^{N(1+R)/4}.(Z_A^{\beta}.Z_B^{\alpha})^{N(1-R)/4}$$

$$= (\pi kT)^{3N/2}.(P_+)^{-3N(1+R)/4}.(P_-)^{-3N(1-R)/4}.$$

The configurational partition function of the assembly is

$$Z = Z_{vib.}.W(R,\sigma).\exp(-E/kT),$$

where $W(R,\sigma)$ is the combinatory factor as calculated in chapters I and III, and E is the configurational energy,

$$E = NzD(r_1-r_o)^2.[\phi-2\phi m+(\phi+1)m^2 - \sigma\{\theta+\phi-2\phi m+(\phi-1)m^2\}]/4$$

$$+ (Nz/4)(V_o'+V_o).$$

The parameters m, θ and ϕ are defined as in chapter III.

The free energy, as a function of the parameters R, σ and m, is obtained from the partition function by the relation $F(R,\sigma,m) = -kT.\ln(Z)$. Thus we have

$$F/N = -(3kT/2)\ln(3\pi kT/zD) + E/N - (kT/N)\ln\{W(R,\sigma)\}$$

$$+(3kT/4)(1+R)\ln\{1 + a(\phi-1)\}$$

$$+(3kT/4)(1-R)\ln\{1 + b(\phi-1)\}. \qquad 5.11$$

Since $\phi \sim 1$ and since a and b have values between 0 and 1, the terms $a(\phi-1)$ and $b(\phi-1)$ are small compared to unity and we may take as a good approximation

$$\ln\{1 + a(\phi-1)\} \doteq a(\phi-1) = (\phi-1)(1-\sigma)/\{2(1+R)\},$$

$$\ln\{1 + b(\phi-1)\} \doteq b(\phi-1) = (\phi-1)(1-\sigma)/\{2(1-R)\}.$$

Also we may omit the first term on the right hand side of equation 5.11 since it will contribute nothing to the order-disorder effect. We remark here that we have already omitted a similar term when we wrote down equation 5.9 without the factor $(2\pi MkT/h^2)^{3/2}$ which is required to make our equations dimensionally correct, but this factor also has no effect on the order-disorder transition. Thus

$$F/N = + E/N - (kT/N)\ln\{W(R,\sigma)\} + (3kT/4)(\phi-1)(1-\sigma).$$

Let $F' = [F/N - \frac{z}{4}(V_o'+V_o)]/\{zD(r_1-r_o)^2\}$. Then, using the expressions for E and $\ln\{W(R,\sigma)\}$ already calculated, we find eventually

$$F' = (1/4)[\phi-2\phi m+(\phi+1)m^2 - \sigma\{\theta+\phi-2\phi m+(\phi-1)m^2\}] \qquad 5.12$$

$$- x[(2/z)\ln 2 + \{1-(1/z)\}\{(1+R)\ln(1+R) + (1-R)\ln(1-R)\}$$

$$- (1/2)(1-\sigma)\ln(1-\sigma) - (1/4)(1+2R+\sigma)\ln(1+2R+\sigma)$$

$$- (1/4)(1-2R+\sigma)\ln(1-2R+\sigma)] + (3x/2z)(\phi-1)(1-\sigma).$$

This expression differs from the similar expression found in chapter III by the presence of the term

$$(3x/2z)(\phi-1)(1-\sigma),$$

so that this term determines the influence of the lattice

vibrations on the order-disorder effect. The particularly simple form of this term, which involves the short range order but not the long range order, is a consequence of the approximation made in putting $\ln\{1 + \frac{a}{b}(\phi-1)\} = \frac{a}{b}(\phi-1)$. This approximation, which seems justified on numerical grounds, was later observed by us to be equivalent to the procedure described by Booth and Rowlinson [43]. In their notation the classical partition function for the motion of an A atom on an α-site is

$$j(w_i)_A = \int_{\text{cell}} \exp\{-E_A^{\alpha}(R_i, w_i)/kT\}.4\pi R_i^2.dR_i,$$

where zw_i is the number of B atoms adjacent to the central A atom, R_i is the distance of the A atom from its mean position, and $E_A^{\alpha}(R_i, w_i)$ is the energy of the A atom when its displacement is R_i. They assume that $\ln\{j(w_i)_A\}$ can be expressed as a linear function of w_i and they write

$$\ln\{j(w_i)_A\} = w_i.\ln(j_1^A) + (1-w_i).\ln(j_o^A).$$

There are several reasonable values which can be given to j_1^A and j_o^A (see for instance, Rowlinson and Curtiss [45]), the simplest being

$$j_1^A = J_{AB}, \qquad j_o^A = J_{AA},$$

where J_{AB} is the partition function for the vibration of an A atom surrounded by B atoms, and J_{AA} is that for an A

atom surrounded by A atoms. The quantity which we have called a is equal to $1-w_i$ so that

$$\ln\{j(a)_A\} = \ln(j_1^A) + a.\ln\{(j_o^A)/(j_1^A)\}$$

$$= \ln(J_{AB}) + a.\ln\{(J_{AA})/(J_{AB})\},$$

which is just what our approximation comes to since

$$J_{AB} = (3\pi kT/zD)^{3/2}$$

$$J_{AA} = (3\pi kT/zD)^{3/2}.\phi^{-3/2}$$

and $\ln(\phi) \doteq \phi-1$ as ϕ will not be very different from unity.

From equation 5.12 we can determine the equilibrium values of R, σ and m as functions of the temperature. Minimising F' with respect to m gives after simplification

$$m = \phi(1-\sigma)/\{\phi+1-\sigma(\phi-1)\},$$

which is the same result as that found in chapter III. The minimisation with respect to R gives eventually

$$\sigma = 2R\{(Z+1)/(Z-1)\} - 1, \qquad Z = \{(1+R)/(1-R)\}^{2(z-1)/z},$$

which also is the same result as that found in chapter III. The minimisation with respect to σ gives eventually

$$x = [\theta + \Phi]/[M - 6(\phi-1)/z],$$

where Φ and M have the same meanings as they had in

chapter III. There we had $x = [\theta + \Phi]/M$, so that the effect of taking account of the lattice vibrations is to subtract $6(\phi-1)/z$ from the denominator, M. Now $M = \infty$ when $R = 1$ and $\sigma = 1$ (i.e. at $x = 0$), so that there is no change from the result of chapter III at the absolute zero. This expresses in mathematical language the fact that the effect of lattice vibrations is negligible at very low temperatures, which is, of course, what we ought to find. M decreases as R and σ decrease and becomes equal to zero when $R = 0$ and $\sigma = 0$. If $\phi > 1$ then $M - 6(\phi-1)/z < M$ and hence x, for a given value of R, is greater than it was in the case where the effect of the lattice vibrations was neglected. That this is reasonable can be seen as follows. (We may state here that taking $V_{AA} = V_{BB}$ involves no loss in generality. If we had taken $D_A \neq D_B$ equation 5.12 would have been unchanged although then ϕ would be defined as the quantity $(\phi_A+\phi_B)/2$. The remarks on pages 34 and 35 apply here.) If $\phi > 1$ then the potential energy function $V_o' + D'(r-r_1)^2$ has a greater slope than the potential energy function $V_o + D(r-r_o)^2$ and therefore has a higher frequency of vibration associated with it. The higher frequency implies a higher energy and thus is energetically less favourable than the lower frequency associated with the A-B pairs. Thus, for $\phi > 1$, energy considerations show that, as far as vibrations are concerned, A-B pairs are

more favourable than A-A or B-B pairs and hence the order in the crystal should be maintained at higher temperatures.

For values of $\phi < 1$ the denominator $M - 6(\phi-1)/z > M$ and thus the value of x, for a given value of R, is less than it was in the case where the effect of the lattice vibrations was not considered. In this case A-B pairs are energetically less favourable, as far as vibrations are concerned, than A-A or B-B pairs and the order of the crystal should decrease more rapidly as the temperature is raised.

If $\phi = 1$ equation 5.13 goes over into equation 3.7. This again is what we would expect since in this case the frequencies of all types of pair are equal. Hence as far as vibration is concerned, no type of pair is energetically more favourable than an other and the vibrations should not affect the order-disorder transition.

In order to demonstrate numerically the effect of taking the lattice vibrations into account we carried out the calculations described in chapter III, using equation 5.12 instead of equation 3.1, for two values of ϕ, one greater than unity and one less than unity. The values of the parameters chosen were ($z = 6$, $\theta = 1$, $\phi = .75$) and ($z = 6$, $\theta = 1$, $\phi = 1.25$). In the following table x_{rest} stands for the values of x when the vibrations are neglected, and x_{vib} for the values from equation 5.13.

TABLE XIII

$z = 6,\ \theta = 1.$

$\phi = .75$

R	σ	$x_{rest.}$	$x_{vib.}$
1.0	1.0	0	0
.95	.9085	1.2564	1.0602
.90	.8268	1.4025	1.1566
.85	.7524	1.4808	1.2031
.80	.6843	1.5270	1.2270
.75	.6219	1.5542	1.2380
.70	.5646	1.5691	1.2410
.65	.5122	1.5757	1.2388

.....

$\phi = 1.25$

R	σ	$x_{rest.}$	$x_{vib.}$
1.0	1.0	0	0
.95	.9085	1.5612	1.9156
.90	.8268	1.6904	2.1468
.85	.7524	1.7360	2.2569
.80	.6843	1.7453	2.3101
.75	.6219	1.7355	2.3308
.70	.5646	1.7150	2.3315

.....

We calculated the transition temperature by the method described and found the following results. In the case $\phi = .75$ the transition temperature was reduced from the value $T_c = 1.559$ obtained in chapter III to the value $T_c = 1.212$. The value of the long range order at the transition temperature was increased from the value $R_- = .736$ to the value $R_- = .836$. Thus in the case $\phi < 1$ the effect of the lattice vibrations is to cause the order of the crystal to decrease more quickly as the temperature is raised, to reduce the transition temperature, and to increase the magnitude of the change at the transition temperature. This last effect, of course, applies strictly only to those transitions which are first order transitions when the lattice vibrations are not taken into account. In fact the tendency of the lattice vibrations in the case $\phi < 1$ is to change the nature of the transition from second order to first order. For instance we found in chapter III that for the case ($z = 6$, $\theta = 2.5$, $\phi = .75$) the transition was a second order one. When we carried out the calculations using equation 5.12 we found that the transition became one of the first order.

In the case $\phi = 1.25$ the transition temperature was increased from the value $T_c = 1.654$ obtained in chapter III to the value $T_c = 2.267$. The value of the long range order just below the transition temperature was reduced

from the value $R_- = .920$ to the value $R_- = .843$. Thus, in the case $\phi > 1$, the effect of the lattice vibrations is to cause the order of the system to decrease more slowly as the temperature is raised, to increase the transition temperature, and to reduce the magnitude of the change at the transition temperature. Here the tendency is to change a first order transition into one of the second order.

The effect of the lattice vibrations on the expansion coefficient and on the specific heat is also easily seen. When $\phi = 1$ the lattice vibrations will not affect the calculation of dm/dx as described in chapter III. When $\phi < 1$ Table III shows that σ changes more quickly with x and hence dm/dx is increased. Thus, in this case, the effect of the lattice vibrations is to increase the calculated values of the expansion coefficient and of the specific heat. Similarly, when $\phi > 1$, the calculated values of the expansion coefficient and of the specific heat are reduced.

It is of interest to compare our results with those of Sarolea [42]) who used the Lennard-Jones 6-12 potential and the Bragg-Williams approximation for the combinatory factor. Sarolea puts

$$V_{XY} = \varepsilon_{XY}[(r_{XY}/r)^{12} - 2(r_{XY}/r)^{6}],$$

and considers the case $r_{AA} = r_{BB} = r_{AB}$. That is, the

volume change effect which she considers is that due to the normal contribution to the thermal expansion, and no account is taken of the contribution which would arise from the differences in the atomic radii of the constituents or from the deviation from the rule of additivity of atomic radii. Our calculations on the other hand have been concerned only with this latter effect. According to Sarolea the effect of including the volume expansion in the Bragg-Williams treatment of the order-disorder transition in AB alloys is to reduce the value of T_c very slightly and to increase the value of C_{p-} from 1.5k to 1.8k per particle. The effect of the lattice vibrations is to reduce the value of T_c by a somewhat greater amount and to increase the value of C_{p-} to about 2k per particle. In the course of the argument, however, Sarolea has to assume $\varepsilon_{AB} > \varepsilon_{AA}$ and $\varepsilon_{AB} > \varepsilon_{BB}$ in order to ensure that certain quantities have the required sign. We do not consider that this assumption is necessarily justified, believing that Figure 16 shows a more plausible representation, so that we do not agree with Sarolea's conclusion that the volume changes and lattice vibrations favour the disappearance of order. We find that the lattice vibrations may or may not favour the disappearance of order depending on the relative sizes of the frequencies of vibration associated with the different types of pair.

We observe that neither Sarolea's results nor those of Booth and Rowlinson [43], who use the more accurate quasi-chemical approximation for the combinatory factor and find the value $C_{p-} = 2.6k$ per particle, give an adequate description of the β-brass transition. Thus the effect of including the lattice vibrations in the theory, though not negligible, bridges only a small part of the gap between theory and experiment. On the other hand we regard the inclusion of a volume change effect which takes explicitly into account the difference in atomic radii of the constituent metals as a necessity for any theory which sets out to give an accurate description of the order-disorder transition in substitutional alloys.

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